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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. *Polit.* lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

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> ———" Cur spirent venti, cur terra dehiscat,
> Cur mare turgescat, pelago cur tantus amaror,
> Cur caput obscura Phœbus ferrugine condat,
> Quid toties diros cogat flagrare cometas,
> Quid pariat nubes, veniant cur fulmina cœlo,
> Quo micet igne Iris, superos quis conciat orbes
> Tam vario motu."
>
> *J. B. Pinelli ad Mazonium.*

ALERE FLAMMAM.

CONTENTS OF VOL. XXXI.

(SIXTH SERIES).

NUMBER CLXXXIII.—MARCH.

NUMBER CLXXXIV.—APRIL.

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PLATES.

I. Illustrative of Messrs. C. V. Raman and S. Appaswamaiyar's Paper on Discontinuous Wave-Motion.

II. Illustrative of Mr. E. J. Evans's Paper on the Absorption Spectra of the Vapours of Inorganic Salts.

ERRATA.

Page 25, the 9th line from bottom should read

P_1, the inward pressure, being proportional to the square of the density, *i. e.* to $\dfrac{1}{(V+b)^2}$, etc.

Page 33, bottom of diagram, instead of Methyl isobutyrate read Ethyl isobutyrate.

Page 33, 6th line from bottom, instead of (A), p. 25, read (A_1), p. 29.

I. *Skating on Thin Ice.*   *By* Sir G. GREENHILL [*].

THIS title is used metaphorically to describe a method of argument which glides so rapidly over the facts as to be able to dispense with their support, but will not bear to be arrested to examine a detail or difficulty.

It is derived from the action of a skater, when he is able to go so fast over ice as to ride on the top of a wave, and to change his place so rapidly as not to allow time to break through, although the ice is not thick enough to support his dead weight at rest.

Analogous action is to be seen in the motion of a bicycle, or of an express train over an elastic bridge.

So, too, a chain in rapid motion, a jet of water, or a gyroscopic flywheel may be hammered with a stick, harder and harder, without flinching to an appreciable extent.

1. The mathematical theory is an extension of Sir William Thomson's investigation in the Philosophical Magazine, November 1871 (reprinted in 'Mathematical and Physical Papers,' vol. iv.), of the propagation of waves and ripples in water, and the tremble of a dewdrop; resumed in Lamb's 'Hydrodynamics,' and by J. R. Wilton, Phil. Mag. May 1915.

Sir W. Thomson shows that the ripples are not propagated below a certain minimum velocity.

———

[*] Communicated by the Author.

The square of the wave-velocity is the sum of two terms : the one due to gravity is proportional to the wave-length ; and the other term is inversely proportional, which depends on the tension of the capillary film.

When the wave-velocity is a minimum these two terms are equal. This should be the velocity of the breeze which begins to ruffle the surface of water, if it were not for the effect of viscosity in the air, which makes a great difference.

Expressed in a mathematical formula, with skin tension T, dynes/cm, water-density ρ, g/cm³, wave-length λ, cm, and wave-velocity U, cm/s, in C.G.S. units,

$$U^2 = \frac{g\lambda}{2\pi} + \frac{2\pi}{\lambda}\frac{T}{\rho} = 2\sqrt{\frac{gT}{\rho}} + \left(\sqrt{\frac{g\lambda}{2\pi}} - \sqrt{\frac{2\pi}{\lambda}\frac{T}{\rho}}\right)^2 ; \quad (1)$$

and U is a minimum U_m, by variation of λ, when the two terms in (1) of U^2 are equal, and then

$$U_m^2 = \frac{g\lambda}{\pi} = \frac{4\pi}{\lambda}\frac{T}{\rho} = 2\sqrt{\frac{gT}{\rho}}, \quad \lambda = 2\pi\sqrt{\frac{T}{g\rho}}. \quad . \quad (2)$$

Thus, if independent experiment, on the tremble of a dewdrop, makes T=74, and we take $g=981$ cm/s², and $\rho=1$ for water, this makes $\lambda=1\cdot73$ cm, and $U_m=23\cdot2$ cm/s, about half a mile an hour, much less than the breeze which ruffles the water, which would be about ten-fold.

The discrepancy is accounted for by viscosity in the air.

2. In the extension to the waves on a sheet of ice of uniform thickness e cm, and modulus of elasticity E g/cm², in gravitation measure, supported on deep water, taken as of the same density ρ, we find ('American Journal of Mathematics,' 1886)

$$U^2 = \frac{\dfrac{g\lambda}{2\pi} + \dfrac{1}{12}\left(\dfrac{2\pi e}{\lambda}\right)^3 \dfrac{gE}{\rho}}{1 + \dfrac{2\pi e}{\lambda}} ; \quad . \quad . \quad . \quad (1)$$

or, putting $\frac{g\lambda}{2\pi} = V^2$, where V is the velocity of wave-length λ on the surface of the clear water, and $\frac{gE}{\rho} = W^2$, so that W is the velocity of longitudinal waves through ice,

$$U^2 = \frac{V^2 + \dfrac{1}{12}\left(\dfrac{ge}{V^2}\right)^3 \dfrac{gE}{\rho}}{1 + \dfrac{ge}{V^2}} = \frac{V^2 + \dfrac{1}{12}\left(\dfrac{ge}{V^2}\right)^3 W^2}{1 + \dfrac{ge}{V^2}} \quad . \quad (2)$$

Neither E nor W is given numerically in the list of Everett's 'Units and Physical Constants,' or in the 'Smithsonian Tables of Physical Constants' either, although it is curious as mathematical history that Ice was the first substance of which the Modulus of Elasticity was defined and measured by Bevan and Young (Phil. Trans. 1826; Todhunter-Pearson, 'History of Elasticity,' p. 189).

3. Thomas Young measures the elasticity of a substance by $\dfrac{E}{\rho}$, a length, k suppose, called the *elastic length*, such that for a small fraction fk of this length, of uniform cross section, hanging vertically, or standing up supported, the material would be stretched or compressed, at the top or bottom end, by an extension or compression f.

Thus a length $\dfrac{k}{100}$ hanging vertically would be stretched one per cent at the top.

Or otherwise, n times the length producing extension $\dfrac{1}{n}$ will give k, the elastic length.

So, too, the tenacity or breaking tension may be defined by the breaking length, as of an icicle; and the stress in the material must be designed in a structure so as to be kept well below the limit of tenacity, for the material to recover itself, and obey the laws of Mathematical Elasticity.

In the 'History of Elasticity' (H. of E.) p. 189, k is taken in feet as 2,100,000—say twenty-five million inches, or two million feet, one-tenth of the value given in Thomson and Tait's 'Natural Philosophy' § 686.

This makes $W = \sqrt{(gk)} = 8000$ f/s, nearly eight times sound-velocity in air; and so explains the story quoted in Ganot's 'Physics' from Parry's 'Arctic Voyages,' where at some distance the sound of the gun fired on the ice was heard before the word of command to fire; the report of the gun being transmitted through the ice and so overtaking the sound through the air and arriving ahead.

So also in an experiment on long-range fire, the report is heard on the telephone long before the sound is transmitted by air. And the crack of a rifle is carried along by a high-velocity bullet, moving faster than ordinary sound, and will be heard up the range a little to one side when the resolved part of the bullet velocity in the direction of the ear is equal to the ordinary sound velocity; the sound through the air from the muzzle is heard appreciably later.

4. The proof of the formula in (1) § 2 is given in a combination of the theory of the elastic lateral vibration of the sheet of ice, propagated in the direction of the waves, with a varying upward pressure δp (gravitation), derived by hydrodynamical theory from the wave-motion in the water below.

Then, if η is the elevation of the ice at a distance x, σ the superficial density in g/cm², and EI the flexure rigidity, in gravitation g/cm,

$$\sigma \frac{d^2\eta}{dt^2} = -g\mathrm{EI}\frac{d^4\eta}{dx^4} + g\delta p, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

$$g\frac{\delta p}{\rho} = \frac{d\phi}{dt} - g\eta, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

ϕ denoting the velocity function of the wave-motion.

Writing m for $\dfrac{2\pi}{\lambda}$, and n for $\dfrac{2\pi\mathrm{U}}{\lambda}$, $\dfrac{n}{m} = \mathrm{U}$, assume

$$\eta = b\sin(mx - nt), \quad \frac{d^2\eta}{dt^2} = -n^2\eta, \quad \frac{d^4\eta}{dx^4} = m^4\eta; \quad (3)$$

and in water of depth h, take

$$\phi = \mathrm{B}\operatorname{ch}m(y+h)\cos(mx-nt), \quad \cdot \quad \cdot \quad (4)$$

so that just under the ice, $y = 0$,

$$\frac{d\phi}{dy} = m\mathrm{B}\operatorname{sh}mh\cos(mx-nt)$$

$$= -\frac{d\eta}{dt} = nb\cos(mx-nt), \quad m\mathrm{B}\operatorname{sh}mh = nb, \quad \cdot \quad \cdot \quad (5)$$

$$\frac{d\phi}{dt} = n\mathrm{B}\operatorname{ch}mh\sin(mx-nt) = \frac{n^2\coth mh}{m}\eta, \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

$$g\frac{\delta p}{\rho} = \left(\frac{n^2}{m}\coth mh - g\right)\eta. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

Substituting in (1), dividing out η,

$$-n^2\sigma = -g\mathrm{EI}m^4 + \frac{n^2}{m}\rho\coth mh - g\rho, \quad \cdot \quad \cdot \quad (8)$$

$$\mathrm{U}^2 = \frac{n^2}{m^2} = \frac{\dfrac{g}{m} + \mathrm{I}m^3\dfrac{g\mathrm{E}}{\rho}}{\coth mh + m\dfrac{\sigma}{\rho}}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

as before in (1) § 2, with

$$\frac{\sigma}{\rho} = e, \quad I = \frac{1}{12}e^3 ;$$

and with

$$V^2 = \frac{g}{m}\,\text{th}\,mh, \quad W^2 = g\frac{E}{\rho} = gk,$$

$$U^2 = \frac{V^2 + \frac{1}{12}(me)^3 W^2\,\text{th}\,mh}{1 + me\,\text{th}\,mh} = \frac{V^2 + \frac{1}{12}\left(\frac{ge}{V^2}\right)^3 W^2\,\text{th}^4\,mh}{1 + \frac{ge}{V^2}\,\text{th}^2\,mh}, \quad (10)$$

in which th mh may be replaced by unity, when the depth h of the water is more than the wave-length λ, making, as in § 2,

$$U^2 = \frac{V^2 + \frac{1}{12}\left(\frac{ge}{V^2}\right)^3 W^2}{1 + \frac{ge}{V^2}}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

5. The determination of the exact minimum value of U^2 in (10) § 4 will lead to an intractable quintic equation, even with th mh replaced by unity in (11) ; but as the term ge/V^2 in the denominator is small, we may consider the variation of U^2 as due to the numerator alone, with th mh omitted as unity,

$$U^2 = V^2 + \frac{1}{12}\left(\frac{ge}{V^2}\right)^3 W^2, \quad \cdot \quad \cdot \quad (1)$$

and this is a minimum by variation of V when

$$V^2 = \frac{1}{4}\left(\frac{ge}{V^2}\right)^3 W^2, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

making

$$U^2 = \frac{4}{3}V^2, \quad \frac{U}{V} = 1\cdot15,$$

that is, U about 15 per cent greater than V.

This is in accordance with the simple theorem that the variation of $ax^m + bx^{-n}$ is zero when its d.c. $max^{m-1} - nbx^{-n-1} = 0$, or $max^m = nbx^{-n}$, and here $m = 1$, $n = 3$.

As another example, the cost per mile of a steamer at K knots being given by the two terms $\frac{A}{K} + BK^2$, it is a minimum when $\frac{A}{K} = 2BK^2$, or with the running expenses and wages twice the coal bill.

A skater, then, who can progress up to this minimum value of U and beyond, is able to place himself at will at any point of the ice-wave he forms, say a little beyond the crest, so as to have the advantage of the downhill; and if the ice should crack he will be able to escape.

Then V has the special value given in (2),

$$\left(\frac{V^2}{ge}\right)^4 = \frac{W^2}{4ge} = \frac{k}{4e}, \quad \frac{\lambda}{2\pi} = \frac{V^2}{g} = \left(\frac{1}{4}ke^3\right)^{\frac{1}{4}} = e\left(\frac{k}{4e}\right)^{\frac{1}{4}}. \quad (3)$$

With the value of k above in § 3, this works out for ice:

	One inch thick.	Two inches thick.
e	$\frac{1}{12}$	$\frac{1}{6}$, foot.
$\lambda = 2\pi\left(\frac{1}{4}ke^3\right)^{\frac{1}{4}}$	26	44, feet.
V	11·5	15, f/s
U	13·2	17·25, f/s
	(9)	(12), m/h

6. But when the depth h is small compared with λ, say $h/\lambda < \frac{1}{2}$, the variation in thmh becomes sensible.

For a value of h still smaller, replacing thmh by mh,

$$V^2 = gh, \quad \frac{U^2}{V^2} = \frac{1 + \left(\frac{2\pi e}{\lambda}\right)^4 \frac{W^2}{12ge}}{1 + m^2 eh} = \frac{1 + \frac{1}{12}\left(\frac{2\pi e}{\lambda}\right)^4 \frac{k}{e}}{1 + \left(\frac{2\pi e}{\lambda}\right)^2 \frac{h}{e}}, \quad (1)$$

and U is large when λ is a fraction of e; but as λ becomes a large multiple of e, U^2 tends to a limit

$$U^2 = \left[1 - \left(\frac{2\pi e}{\lambda}\right)^2 \frac{h}{e}\right]gh; \quad . \quad . \quad . \quad (2)$$

so that a long flat wave in ice of thickness e on water of uniform depth h will have velocity

$$\left[1 - \frac{1}{2}\left(\frac{2\pi e}{\lambda}\right)^2 \frac{h}{e}\right]\sqrt{(gh)}.$$

7. The value of E and k was determined experimentally by B. Bevan (Phil. Trans. 1826, H. of E. p. 189) with a cantilever of ice, cut out as a tongue except for one end; of

length l (100 inches), breadth b (10 inches), thickness e (4 inches).

Working with the inch as unit of length, the bending moment equation is

$$EAK^2\frac{d^2\eta}{dx^2} = \rho A(l-x)\frac{l+x}{2}, \quad . \quad . \quad . \quad . \quad (1)$$

from which the cross section $A = be$ divides out, and where $K^2 = \frac{1}{12}e^2$; so that with $E/\rho = k$, inches,

$$\frac{1}{12}ke^2\frac{d^2\eta}{dx^2} = \frac{1}{2}(l^2 - x^2), \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{1}{12}ke^2\frac{d\eta}{dx} = \frac{1}{2}\left(l^2 x - \frac{1}{3}x^3\right), \quad . \quad . \quad . \quad . \quad (3)$$

$$\frac{1}{12}ke^2\eta = \frac{1}{2}\left(\frac{1}{2}l^2 x^2 - \frac{1}{12}x^4\right); \quad . \quad . \quad . \quad (4)$$

and if d denotes the droop at the end, where $x = l$,

$$\frac{1}{12}ke^2 d = \frac{1}{4}l^4 - \frac{1}{24}l^4 = \frac{5}{24}l^4, \quad d = \frac{5l^4}{2ke^2}. \quad . \quad . \quad (5)$$

Thus with $l = 100$, $e = 4$, $k = 25$ million, inches, we find

$$d = 0.625, \quad \text{say } \tfrac{2}{3} \text{ inch.} \quad . \quad . \quad . \quad . \quad (6)$$

And conversely, this value of d measured would lead to the value of k above.

8. The skin stress on the top or bottom of the ice, given by an equivalent length h as ρh, is such that the bending moment is due to an average tension or pressure $\frac{1}{2}\rho h$, acting over $\frac{1}{2}be$, the upper or lower half of the cross section, at a distance $\frac{1}{3}e$ from the neutral mean line, and is therefore

$$\frac{1}{2}\rho h \times \frac{1}{2}be \times \frac{1}{3}e \times 2 = \frac{1}{6}\rho hbe^2 = \frac{1}{6}\rho hAe = \frac{1}{2}\rho A(l^2 - x^2), \quad (1)$$

$$h = 3\frac{l^2 - x^2}{e}, \quad \text{a maximum } \frac{3l^2}{e} \text{ at O;} \quad . \quad . \quad (2)$$

so that in the experiment

$$h = \frac{30000}{4} = 7500 \text{ inches, or } 625 \text{ feet,} \quad . \quad . \quad (3)$$

as of an icicle of uniform cross section; and it is not likely the ice could stand it without breaking.

But in Bevan's experiment the tongue of ice was left supported on the water, and deflected by a weight at the free end ; and then, if the ice was deflected d inches by a weight of P lb at a distance a from the root, in a tongue b inches broad and e thick,

$$\text{EI}d = \frac{1}{12}\rho ke^3 bd = \frac{1}{3}\text{P}a^3, \quad k = \frac{4\text{P}a^3}{\rho e^3 bd}, \quad \cdot \quad \cdot \quad (4)$$

in accordance with the usual formula.

In an experiment, P=25, a=98, b=10, e=4, and by measurement d=0·206 inch; so that with a specific volume of ice or water $\frac{1}{\rho}$ = 27·73 inch³/lb,

$$k = \frac{4 \times 25 \times 27\cdot73 \times 98^3}{4^3 \times 10 \times 0\cdot206} \text{ inches, } \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

and this works out to about 20 million.

Then for the skin stress, ρh,

$$\frac{1}{6}\rho he^2 b = \text{P}a = \frac{\rho ke^3 bd}{4a^2}, \quad \frac{h}{k} = \frac{3ed}{2a^2}, \quad \cdot \quad \cdot \quad (6)$$

and this works out to

$$\frac{h}{k} = 0\cdot00012, \quad h = 3000 \text{ inches, 250 feet, } \quad \cdot \quad \cdot \quad (7)$$

still rather long for an icicle.

9. Pack ice is produced by thrust in the surface. Estimated at a pressure P=ρc, the D.E. (1) § 4 is modified into

$$\sigma\frac{d^2\eta}{dt^2} = -g\text{EI}\frac{d^4\eta}{dx^4} - g\text{P}e\frac{d^2\eta}{dx^2} + g\delta p, \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

and for ice at rest, $\frac{d^2\eta}{dt^2}$=0, $\delta p = -\rho\eta$,

$$\text{EI}\frac{d^4\eta}{dx^4} + \text{P}e\frac{d^2\eta}{dx^2} + \rho\eta = 0, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

$$\frac{1}{12}ke^3\frac{d^4\eta}{dx^4} + ce\frac{d^2\eta}{dx^2} + \eta = 0. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

Here the sign of P and c would be changed for a superficial tension, as of the capillary film in § 1, or a cloth on the surface.

With a solution $\eta = e^{mxi}$, the auxiliary equation (A.E.) of (2) becomes

$$\frac{1}{12} ke^3 m^4 - cem^2 + 1 = 0, \quad \ldots \ldots \quad (4)$$

$$\left(\frac{1}{m^2} - \frac{1}{2} ce \right)^2 = \frac{1}{4} e^2 \left(c^2 - \frac{1}{3} ke \right), \quad \ldots \quad (5)$$

requiring

$$c^2 > \frac{1}{3} ke, \quad P > \rho \sqrt{\left(\frac{1}{3} ke \right)} > \rho \sqrt{\frac{eW^2}{3g}}, \quad \ldots \quad (6)$$

for the ice to become unstable, and the surface to buckle up into waves.

The vibration equation in (8) § 4 can be adjusted so as to introduce the term due to P : it makes

$$-n^2 \sigma = -gEIm^4 + gPem^2 + \frac{n^2}{m} \rho \coth mh - g\rho, \quad \ldots \quad (7)$$

$$\frac{U^2}{g} = \frac{n^2}{gm^2} = \frac{\dfrac{1}{m} - \dfrac{P}{\rho} em + \dfrac{E}{\rho} Im^3}{\coth mh + m \dfrac{\sigma}{\rho}}$$

$$= \frac{\dfrac{1}{m} - cem + \dfrac{1}{12} ke^3 m^3}{\coth mh + me} = \frac{1 - cem^2 + \dfrac{1}{12} ke^3 m^4}{m \coth mh + em^2}; \quad (8)$$

but the extra complication does not repay investigation.

10. For the deflexion of ice at rest, bent into a cylindrical surface of straight waves, by a single line-load over O, such as a log, equation (1) § 4 becomes

$$EI \frac{d^4 \eta}{dx^4} = \delta p = -\rho \eta, \quad \ldots \ldots \quad (1)$$

$$\frac{1}{\eta} \frac{d^4 \eta}{dx^4} = -\frac{12}{ke^3} = -4q^4, \quad \frac{1}{12} ke^3 = \frac{1}{4q^4}, \quad \frac{1}{q} = \left(\frac{1}{3} ke^3 \right)^{\frac{1}{4}}, \quad (2)$$

suppose; so that q is the reciprocal of a length, and for positive x and η finite the solution is

$$\eta = e^{-qx} (A \cos qx + B \sin qx). \quad \ldots \quad (3)$$

To make $\dfrac{d\eta}{dx} = 0$ at $x = 0$, $A = B$; and measuring η upward,

$$\eta = -ae^{-qx} (\cos qx + \sin qx), \quad \ldots \ldots \quad (4)$$

$$\frac{d\eta}{dx} = 2aqe^{-qx} \sin qx, \qquad \frac{d^2\eta}{dx^2} = 2aq^2 e^{-qx} (\cos qx - \sin qx),$$

$$\frac{d^3\eta}{dx^3} = -4aq^3 e^{-qx} \cos qx, \quad \int \eta \, dx = \frac{a}{q} e^{-qx} \cos qx. \quad \ldots \quad (5)$$

The area displaced between the water-line and profile of the ice is then

$$\int_0 -\eta dx = \frac{a}{q}(1 - e^{-qx}\cos qx), \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

and this area up to infinity is $\frac{a}{q}$.

The ice is deflected into two cylindrical surfaces, symmetrical on each side of O; and if the line-load over O is W per unit length, it is buoyed up by the displacement $\frac{2a}{q}$ of water; and

$$\frac{2a\rho}{q} = W, \quad a = \frac{1}{2}\frac{Wq}{\rho} = \frac{W}{2\rho\left(\frac{1}{3}ke^3\right)^{\frac{1}{4}}} = \frac{W}{2\rho e}\left(\frac{3e}{k}\right)^{\frac{1}{4}} \cdot \cdot \quad (7)$$

The bending moment (B.M.) of the ice is a maximum under O, and is

$$EI\frac{d^2\eta}{dx^2} = \rho k\frac{1}{12}e^3 2aq^2 = \frac{1}{12}ke^3q^3 W = \frac{1}{4}\frac{W}{q} = \frac{1}{4}\left(\frac{1}{3}ke^3\right)^{\frac{1}{4}}W. \quad (8)$$

The maximum skin stress of the ice has then a tension or pressure length h, such that

$$\frac{1}{6}\rho he^2 = \text{max. B.M.} = \frac{1}{6}\rho ke^3 aq^2, \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

$$\frac{h}{a} = keq^2 = \left(\frac{3k}{e}\right)^{\frac{1}{2}} = \frac{8660}{\sqrt{e}}, \quad h = \frac{3W}{2\rho e}\left(\frac{k}{3e}\right)^{\frac{1}{4}} \cdot \cdot \quad (10)$$

The shearing force F at a distance x is then given by

$$2F = W - \frac{2\rho a}{q}(1 - e^{-qx}\cos qx) = \frac{2\rho a}{q}e^{-qx}\cos qx$$

$$= -2\frac{d}{dx}\text{ (B.M.)}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

as a verification.

11. A central line-load W at the middle O of a plank or beam, of limited length $2l$, floating on water, will give a downward deflexion η such that, from x to l,

$$EI\frac{d^2\eta}{dx^2} + \rho\int_x^l (x' - x)\eta' dx' = 0, \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

$$EI\frac{d^3\eta}{dx^3} - \rho\int_x^l \eta' dx' \qquad = 0, \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

$$EI\frac{d^4\eta}{dx^4} + \rho\eta \qquad\qquad = 0, \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

as before in (1) § 10, with a solution

$$\eta = B_1 \operatorname{ch} qx \cos qx + B_2 \operatorname{sh} qx \sin qx, \quad . \quad . \quad (4)$$

to satisfy the condition of symmetry on each side of O.

The bending moment at the free end of the beam is zero, and so at $x = \pm l$,

$$\frac{d^2\eta}{dx^2} = -2B_1 q^2 \operatorname{sh} ql \sin ql + 2B_2 q^2 \operatorname{ch} ql \cos ql = 0, \quad (5)$$

and we put

$$\eta = C\left(\frac{\operatorname{ch} qx \cos qx}{\operatorname{sh} ql \sin ql} + \frac{\operatorname{sh} qx \sin qx}{\operatorname{ch} ql \cos ql}\right). \quad . \quad . \quad (6)$$

The load W is supported by the extra buoyancy due to the downward displacement η; so that

$$W = \int_{-l}^{l} \rho\eta \, dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which

$$\int_{0}^{l} q \operatorname{ch} qx \cos qx \, dx = \tfrac{1}{2}(\quad \operatorname{sh} ql \cos ql + \operatorname{ch} ql \sin ql), \quad (8)$$

$$\int q \operatorname{sh} qx \sin qx \, dx = \tfrac{1}{2}(-\operatorname{sh} ql \cos ql + \operatorname{ch} ql \sin ql), \quad (9)$$

$$W = \rho \frac{C}{q}\left(\frac{\operatorname{sh} ql \cos ql + \operatorname{ch} ql \sin ql}{\operatorname{sh} ql \sin ql} + \frac{-\operatorname{sh} ql \cos ql + \operatorname{ch} ql \sin ql}{\operatorname{ch} ql \cos ql}\right)$$

$$= \rho \frac{C}{q}\left(\frac{1}{\sin ql \cos ql} + \frac{1}{\operatorname{sh} ql \operatorname{ch} ql}\right) = \frac{2\rho C}{q}\left(\frac{1}{\sin 2ql} + \frac{1}{\operatorname{sh} 2ql}\right); \quad (10)$$

so that if a was the extra draft of the plank due to the load W distributed uniformly over the upper surface, $W = 2\rho la$,

$$C = aql \frac{\operatorname{sh} 2ql \sin 2ql}{\operatorname{sh} 2ql + \sin 2ql}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\frac{\eta}{a} = 4ql \frac{\operatorname{ch} ql \cos ql \operatorname{ch} qx \cos qx + \operatorname{sh} ql \sin ql \operatorname{sh} qx \sin qx}{\operatorname{sh} 2ql + \sin 2ql}. \quad (12)$$

12. With a series of parallel line-loads, W, at equal interval $2l$, the surface of the ice will be bent into equal waves joined together, given between $x = \pm l$ by the general solution of (4) § 11, with the origin O midway between two consecutive loads; and with symmetry in the wave on each

side of O, and with a change to measuring η downward,

$$\text{EI}\frac{d^4\eta}{dx^4}+\rho\eta = 0, \quad \frac{1}{12}ke^3\frac{d^4\eta}{dx^4}+\eta = 0, \quad . \quad . \quad (1)$$

$$\eta = \text{A ch } qx \cos qx + \text{B sh } qx \sin qx ; \quad . \quad . \quad (2)$$

and to satisfy the condition $\frac{d\eta}{dx}=0$ when $x=\pm l,$

$$\eta = a[\text{ch }q(l+x)\sin q(l-x)+\text{ch }q(l-x)\sin q(l+x)$$
$$+\text{sh }q(l+x)\cos q(l-x)+\text{sh }q(l-x)\cos q(l+x)], . \ (3)$$

$$\frac{d\eta}{dx}= 2qa[\text{sh }q(l+x)\sin q(l-x)-\text{sh }q(l-x)\sin q(l+x)], \ (4)$$

with an area for buoyancy,

$$\frac{\text{W}}{\rho} = \int_{-l}^{l}\eta\,dx = 2\frac{a}{q}\,(\text{ch }2ql-\cos 2ql). \quad . \quad . \quad (5)$$

When
$$x = 0, \quad \eta_0 = 2a(\text{ch }ql\sin ql+\ \text{sh }ql\cos ql),$$
$$x = \pm l, \quad \eta_l = 2a(\text{ch }ql\text{ sh }\ ql+\cos ql\sin ql),$$

and putting $\text{W}=2lw$, so that w is the average superficial loading, which we may reckon in lb/inch^2,

$$\eta_0 = \frac{2w}{\rho}\ \frac{ql(\text{ch }ql\sin ql+\text{sh }ql\cos ql)}{\text{ch }2ql-\cos 2ql}, \quad . \quad . \quad (6)$$

$$\eta_l = \frac{2w}{\rho}\ \frac{ql(\text{ch }ql\text{ sh }ql+\cos ql\sin ql)}{\text{ch }2ql-\cos 2ql}, \quad . \quad . \quad (7)$$

reducing in each case when $ql=0$ to

$$\eta_0 = \eta_l = w/\rho = b, \quad . \quad . \quad . \quad . \quad (8)$$

the uniform depression of the ice when the load is distributed uniformly.

Equation (8) (10) § 10 of the B.M. at O, and skin stress, is changed to a maximum

$$\text{E }\frac{1}{12}\,e^3 2q^2\text{B}= \frac{1}{6}\,ke^3q^3\text{W }\frac{\text{ch }ql\sin ql-\text{sh }ql\cos ql}{\text{ch }2ql-\cos 2ql} =\frac{1}{6}\rho he^2, \ (9)$$

$$\frac{h}{a} = 2keq^2\,(\text{ch }ql\sin ql-\text{sh }ql\cos ql). \quad . \quad . \quad (10)$$

In this way the relation can be calculated between the thickness of the ice and the loading permissible, distributed as infantry or artillery.

13. Next, roll the logs in a regular procession at velocity **U** and equal interval $2l$, to represent the passage for instance

of a train of artillery, with the ice in waves advancing underneath at the same rate.

Or else reduce to a steady motion by giving the ice and water underneath a reversed velocity U, with the logs now stationary, and $\dfrac{d^2\eta}{dt^2}$ replaced by $U^2\dfrac{d^2\eta}{dx^2}$.

Then, with no pack-thrust P,

$$\sigma\,\frac{U^2}{g}\frac{d^2\eta}{dx^2} = -\,EI\frac{d^4\eta}{dx^4} + \delta p, \quad \cdots \quad (1)$$

$$\frac{\delta p}{\rho} + \eta + \frac{u^2 - U^2}{2g} = 0, \quad \cdots \quad (2)$$

$$EI\frac{d^4\eta}{dx^4} + \sigma\,\frac{U^2}{g}\frac{d^2\eta}{dx^2} + \rho\eta + \rho\frac{u^2 - U^2}{2g} = 0; \quad \cdots \quad (3)$$

and with $E = \rho k$, $I = \frac{1}{12}e^3$, $\sigma = \rho e$,

$$\frac{1}{12}\,ke^3\frac{d^4\eta}{dx^4} + e\frac{U^2}{g}\frac{d^2\eta}{dx^2} + \eta + \frac{u^2 - U^2}{2g} = 0. \quad \cdots \quad (4)$$

Measuring y and η upward, the velocity function

$$\phi = Ux + A_1\phi_1 + A_2\phi_2, \quad \cdots \quad (5)$$

$$\left.\begin{aligned} u &= -\frac{d\phi}{dx} = -U - A_1\frac{d\phi_1}{dx} - A_2\frac{d\phi_2}{dx}, \\ \frac{u^2 - U^2}{2g} &= \frac{U}{g}\left(A_1\frac{d\phi_1}{dx} + A_2\frac{d\phi_2}{dx}\right), \end{aligned}\right\} \quad \cdots \quad (6)$$

to the first order, where ϕ_1, ϕ_2 are composed of terms of the form $e^{(a+bi)(x+yi)}$; and taking the water deep, so that ϕ_1, ϕ_2 are zero for $y = -\infty$, we put

$$\phi_1 = e^{ax+by}\cos(ay - bx + h_1), \quad \phi_2 = e^{-ax+by}\cos(ay + bx + h_2), \quad (7)$$

for each stretch of water between two logs, with some slight discontinuity at a vertical plane of junction, of vertical slipping without cavitation, which may be ignored; and then

$$\nabla^2(\phi_1, \phi_2) = 0,$$

satisfying the Equation of Continuity.

With the origin midway between two logs, take

$$\eta = B_1\eta_1 + B_2\eta_2, \quad \cdots \quad (8)$$

$$\eta_1 = \text{ch } ax \cos bx, \quad \eta_2 = \text{sh } ax \sin bx, \quad \cdots \quad (9)$$

and put

$$\eta_3 = \text{sh } ax \cos bx, \quad \eta_4 = \text{ch } ax \sin bx. \quad \cdots \quad (10)$$

Then, with $a = c \cos \alpha$, $b = c \sin \alpha$,

$$\frac{1}{c}\frac{d\eta_1}{dx} = \eta_3 \cos \alpha - \eta_4 \sin \alpha, \qquad \frac{1}{c}\frac{d\eta_2}{dx} = \eta_3 \sin \alpha + \eta_4 \cos \alpha, \quad (11)$$

$$\frac{1}{c}\frac{d\eta_3}{dx} = \eta_1 \cos \alpha - \eta_2 \sin \alpha, \qquad \frac{1}{c}\frac{d\eta_4}{dx} = \eta_1 \sin \alpha + \eta_2 \cos \alpha, \quad (12)$$

$$c\eta_1 = \frac{d\eta_3}{dx}\cos \alpha + \frac{d\eta_4}{dx}\sin \alpha, \qquad c\eta_2 = -\frac{d\eta_3}{dx}\sin \alpha + \frac{d\eta_4}{dx}\cos \alpha, \quad (13)$$

$$\int c\eta_1 dx = \eta_3 \cos \alpha + \eta_4 \sin \alpha, \qquad \int c\eta_2 dx = -\eta_3 \sin \alpha + \eta_4 \cos \alpha. \quad (14)$$

$$\frac{1}{c^2}\frac{d^2\eta_1}{dx^2} = \eta_1 \cos 2\alpha - \eta_2 \sin 2\alpha, \qquad \frac{1}{c^4}\frac{d^4\eta_1}{dx^4} = \eta_1 \cos 4\alpha - \eta_2 \sin 4\alpha, \quad (15)$$

$$\frac{1}{c^2}\frac{d^2\eta_2}{dx^2} = \eta_1 \sin 2\alpha + \eta_2 \cos 2\alpha, \qquad \frac{1}{c^4}\frac{d^4\eta_2}{dx^4} = \eta_1 \sin 4\alpha + \eta_2 \cos 4\alpha, \quad (16)$$

$$\frac{1}{c^2}\frac{d^2\eta_3}{dx^2} = \eta_3 \cos 2\alpha - \eta_4 \sin 2\alpha, \qquad \frac{1}{c^4}\frac{d^4\eta_3}{dx^4} = \eta_3 \cos 4\alpha - \eta_4 \sin 4\alpha, \quad (17)$$

$$\frac{1}{c^2}\frac{d^2\eta_4}{dx^2} = \eta_3 \sin 2\alpha + \eta_4 \cos 2\alpha, \qquad \frac{1}{c^4}\frac{d^4\eta_4}{dx^4} = \eta_3 \sin 4\alpha + \eta_4 \cos 4\alpha. \quad (18)$$

Just under the ice, where $y = 0$,

$$\frac{d\phi}{dy} = U\frac{d\eta}{dx}, \quad A_1\frac{d\phi_1}{dy} + A_2\frac{d\phi_2}{dy} = UB_1\frac{d\eta_1}{dx} + UB_2\frac{d\eta_2}{dx}, \quad \cdots \quad (19)$$

$$\frac{1}{c}\frac{d\phi_1}{dy} = e^{ax}\cos(-bx + h_1)\sin \alpha - e^{ax}\sin(-bx + h_1)\cos \alpha$$

$$= e^{ax}\sin(bx - h_1 + \alpha)$$

$$= (\operatorname{ch} ax + \operatorname{sh} ax)[\sin bx \cos(h_1 - \alpha) - \cos bx \sin(h_1 - \alpha)]$$

$$= (\eta_2 + \eta_4)\cos(h_1 - \alpha) - (\eta_1 + \eta_3)\sin(h_1 - \alpha), \quad \cdots \quad (20)$$

$$\frac{1}{c}\frac{d\phi_2}{dy} = e^{-ax}\cos(bx + h_2)\sin \alpha - e^{-ax}\sin(bx + h_2)\cos \alpha$$

$$= e^{-ax}\sin(-bx - h_2 + \alpha)$$

$$= (\operatorname{ch} ax - \operatorname{sh} ax)[-\sin bx \cos(h_2 - \alpha) - \cos bx \sin(h_2 - \alpha)]$$

$$= (\eta_2 - \eta_4)\cos(h_2 - \alpha) - (\eta_1 - \eta_3)\sin(h_2 - \alpha). \quad \cdots \quad (21)$$

But η_1 and η_2 are absent in $\dfrac{d\eta_1}{dx}$, $\dfrac{d\eta_2}{dx}$, and so must be absent in $A_1 \dfrac{d\phi_1}{dy} + A_2 \dfrac{d\phi_2}{dy}$, so that

$$A_1 \cos(h_1 - \alpha) + A_2 \cos(h_2 - \alpha) \text{ and } A_1 \sin(h_1 - \alpha) + A_2 \sin(h_2 - \alpha) = 0, \quad (22)$$

$$\frac{A_1}{A_2} = -\frac{\cos(h_2 - \alpha)}{\cos(h_1 - \alpha)} = -\frac{\sin(h_2 - \alpha)}{\sin(h_1 - \alpha)}, \quad \tan(h_1 - \alpha) = \tan(h_2 - \alpha),$$

$$h_1 = h_2 = h, \quad A_1 = -A_2 = A, \quad \ldots \ldots (23)$$

$$A_1 \frac{d\phi_1}{dy} + A_2 \frac{d\phi_2}{dy} = -2Ac\eta_3 \sin(h - \alpha) + 2Ac\eta_4 \cos(h - \alpha)$$

$$= UB_1 \frac{d\eta_1}{dx} + UB_2 \frac{d\eta_2}{dx}$$

$$= UB_1 c(\eta_3 \cos\alpha - \eta_4 \sin\alpha) + UB_2 c(\eta_3 \sin\alpha + \eta_4 \cos\alpha), \quad \ldots (24)$$

$$\left.\begin{array}{l} UB_1 \cos\alpha + UB_2 \sin\alpha = -2A \sin(h - \alpha), \\ UB_1 \sin\alpha - UB_2 \cos\alpha = -2A \cos(h - \alpha), \end{array}\right\} \quad \ldots \ldots (25)$$

$$UB_1 = -2A \sin h, \qquad UB_2 = 2A \cos h, \quad \ldots \ldots (26)$$

$$\phi = Ux + A(\phi_1 - \phi_2)$$

$$= Ux + Ae^{by}(\operatorname{ch} ax + \operatorname{sh} ax)[\cos bx \cos(ay + h) + \sin bx \sin(ay + h)]$$

$$\quad - Ae^{by}(\operatorname{ch} ax - \operatorname{sh} ax)[\cos bx \cos(ay + h) - \sin bx \sin(ay + h)]$$

$$= Ux + Ce^{by}\eta_3 \cos(ay + h) + Ce^{by}\eta_4 \sin(ay + h), \quad \ldots \ldots (27)$$

with

$$2A = C, \quad UB_1 = -C \sin h, \quad UB_2 = C \cos h, \quad \ldots (28)$$

$$U\eta = C(-\eta_1 \sin h + \eta_2 \cos h), \quad \ldots \ldots \ldots (29)$$

$$\frac{U}{Cc^2}\frac{d^2\eta}{dx^2} = (-\eta_1 \cos 2\alpha + \eta_2 \sin 2\alpha)\sin h + (\eta_1 \sin 2\alpha + \eta_2 \cos 2\alpha)\cos h$$

$$= \eta_1 \sin(2\alpha - h) + \eta_2 \cos(2\alpha - h), \quad \ldots \ldots (30)$$

$$\frac{U}{Cc^4}\frac{d^4\eta}{dx^4} = \eta_1 \sin(4\alpha - h) + \eta_2 \cos(4\alpha - h), \quad \ldots \ldots (31)$$

From (27) when $y = 0$,

$$A_1 \frac{d\phi_1}{dx} + A_2 \frac{d\phi_2}{dx} = Cc[\eta_1 \cos(h - \alpha) + \eta_2 \sin(h - \alpha)]. \quad \ldots \ldots (32)$$

Substitute in the dynamical equation (4), and divide out C, using (6),

$$\frac{1}{12}ke^3c^4[\eta_1\sin(4\alpha-h)+\eta_2\cos(4\alpha-h)]$$

$$+e\frac{U^2}{g}c^2[\eta_1\sin(2\alpha-h)+\eta_2\cos(2\alpha-h)]-\eta_1\sin h+\eta_2\cos h$$

$$+\frac{U^2}{g}c[\eta_1\cos(\alpha-h)-\eta_2\sin(\alpha-h)]=0,\quad\ldots\quad(33)$$

and equating to zero the coefficients of η_2 and η_1,

$$\frac{1}{12}ke^3c^4\cos(4\alpha-h)+e\frac{U^2}{g}c^2\cos(2\alpha-h)+\cos h-\frac{U^2}{g}c\sin(\alpha-h)=0,\quad(34)$$

$$\frac{1}{12}ke^3c^4\sin(4\alpha-h)+e\frac{U^2}{g}c^2\sin(2\alpha-h)-\sin h+\frac{U^2}{g}c\cos(\alpha-h)=0,\quad(35)$$

$$-\tan h=\frac{\frac{1}{12}ke^3c^4\cos4\alpha+e\frac{U^2}{g}c^2\cos2\alpha-\frac{U^2}{g}c\sin\alpha+1}{\frac{1}{12}ke^3c^4\sin4\alpha+e\frac{U^2}{g}c^2\sin2\alpha+\frac{U^2}{g}c\cos\alpha},\quad\ldots\quad(36)$$

$$\tan h=\frac{\frac{1}{12}ke^3c^4\sin4\alpha+e\frac{U^2}{g}c^2\sin2\alpha+\frac{U^2}{g}c\cos\alpha}{\frac{1}{12}ke^3c^4\cos4\alpha+e\frac{U^2}{g}c^2\cos2\alpha-\frac{U^2}{g}c\sin\alpha+1},\quad\ldots\quad(37)$$

$$\left(\frac{1}{12}ke^3c^4\cos4\alpha+e\frac{U^2}{g}c^2\cos2\alpha-\frac{U^2}{g}c\sin\alpha+1\right)^2$$

$$+\left(\frac{1}{12}ke^3c^4\sin4\alpha+e\frac{U^2}{g}c^2\sin2\alpha+\frac{U^2}{g}c\cos\alpha\right)^2=0,\quad\ldots\quad(38)$$

$$\frac{1}{12}ke^3c^4\cos4\alpha+e\frac{U^2}{g}c^2\cos2a-\frac{U^2}{g}c\sin\alpha+1=0,\quad\ldots\quad(39)$$

$$\frac{1}{12}ke^3c^4\sin4\alpha+e\frac{U^2}{g}c^2\sin2\alpha+\frac{U^2}{g}c\cos\alpha=0,\quad\ldots\quad(40)$$

$$\frac{1}{12}ke^3(a+bi)^4+e\frac{U^2}{g}(a+bi)^2+i\frac{U^2}{g}(a+bi)+1=0.\quad\ldots\quad(41)$$

Then, with $a+bi=im$,

$$\frac{1}{12}ke^3m^4-e\frac{U^2}{g}m^2-\frac{U^2}{g}m+1=0,\quad\ldots\quad(42)$$

$$\frac{U^2}{g}=\frac{\frac{1}{m}+\frac{1}{12}ke^3m^3}{1+em},\quad\ldots\quad(43)$$

as before in (9) § 4, in deep water, with $\coth mh=1$.

Introducing the condition

$$x = \pm l, \quad \frac{d\eta}{dx} = 0, \quad -\frac{d\eta_1}{dx}\sin h + \frac{d\eta_2}{dx}\cos h = 0,$$

$$-(\eta_3\cos\alpha - \eta_4\sin\alpha)\sin h + (\eta_3\sin\alpha + \eta_4\cos\alpha)\cos h = 0,$$

$$\eta_3\sin(\alpha - h) + \eta_4\cos(\alpha - h) = 0, \quad \cdot \quad \cdot \quad \cdot \quad (44)$$

$$\tan(h - \alpha) = \frac{\eta_4}{\eta_3} = \frac{\operatorname{ch} al \sin bl}{\operatorname{sh} al \cos bl} = \frac{\tan bl}{\operatorname{th} al}, \quad \cdot \quad \cdot \quad (45)$$

$$\frac{\sin(h-\alpha)}{\operatorname{ch} al \sin bl} = \frac{\cos(h-\alpha)}{\operatorname{sh} al \cos bl} = \frac{1}{\sqrt{(2 \cdot \operatorname{ch} 2al - \cos 2bl)}}, \quad \cdot \quad (46)$$

$$\eta_3 = \sqrt{(\tfrac{1}{2} \cdot \operatorname{ch} 2al - \cos 2bl)}\cos(h-\alpha),$$

$$\eta_4 = \sqrt{(\tfrac{1}{2} \cdot \operatorname{ch} 2al - \cos 2bl)}\sin(h-\alpha), \quad \cdot \quad \cdot \quad (47)$$

at $x = \pm l$.

The extra buoyancy over the length $2l$, required for the load W, is given by

$$W = \int_{-l}^{l} -\rho\eta\, dx = \frac{2C\rho}{Uc}\int_{0}^{l}(c\eta_1\sin h - c\eta_2\cos h)\, dx$$

$$= \frac{2C\rho}{Uc}\left[(\eta_3\cos\alpha + \eta_4\sin\alpha)\sin h - (-\eta_3\sin\alpha + \eta_4\cos\alpha)\cos h\right]$$

$$= \frac{2C\rho}{Uc}\left[\eta_3\sin(h+\alpha) - \eta_4\cos(h+\alpha)\right]$$

$$= \frac{C\rho}{Uc}\sin 2\alpha\sqrt{(2 \cdot \operatorname{ch} 2al - \cos 2bl)}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (48)$$

which determines C.

14. If the extra buoyancy of the water is taken into account in Bevan's experiment of § 8, where the tongue of ice is depressed into the water by the weight applied at the free end, we take

$$\eta = B_1\eta_1 + B_2\eta_2 + B_3\eta_3 + B_4\eta_4, \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

and the condition $\eta = 0$, $\frac{d\eta}{dx} = 0$, at $x = 0$, requires, since $a = b$,

$$B_1 = 0, \qquad B_3 + B_4 = 0,$$

$$\eta = B_2\eta_2 + B_3(\eta_3 - \eta_4). \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

Here $a = b = q$,

$$\frac{1}{q^2}\frac{d^2\eta_1}{dx^2} = -2\eta_2, \quad \frac{1}{q^2}\frac{d^2\eta_2}{dx^2} = 2\eta_1, \quad \frac{1}{q^2}\frac{d^2\eta_3}{dx^2} = -2\eta_4, \quad \frac{1}{q^2}\frac{d^2\eta_4}{dx^2} = 2\eta_3, \quad (3)$$

$$\frac{1}{q^2}\frac{d^2\eta}{dx^2} = 2B_2\eta_1 + B_3(-2\eta_4 - 2\eta_3) = 0, \text{ when } x = l, \quad . \quad . \quad . \quad . \quad (4)$$

$$\left. \begin{array}{c} B_2 \operatorname{ch} ql \cos ql - B_3(\operatorname{sh} ql \cos ql + \operatorname{ch} ql \sin ql) = 0, \\ \dfrac{B_2}{B_3} = \operatorname{th} ql + \tan ql. \end{array} \right\} \quad . \quad . \quad (5)$$

At $x = 0$, and measuring η downward,

$$\frac{1}{12}\rho k e^3 b \frac{d^2\eta}{dx^2} = \frac{1}{12}\rho k e^3 b \cdot 2q^2 B_2$$

$$= \text{bending moment at } O = Pl - \rho b \int_0^l x\eta \, dx, \quad . \quad (6)$$

and integrating by parts,

$$\int x\eta \, dx = x\int \eta \, dx - \iint \eta \, dx, \quad . \quad . \quad . \quad . \quad (7)$$

in which

$$\int q\eta_1 dx \quad = \tfrac{1}{2}(\eta_3 + \eta_4), \qquad \iint q^2\eta_1 dx \quad = \tfrac{1}{2}\eta_2, \quad . \quad . \quad . \quad (8)$$

$$\int q\eta_2 dx \quad = \tfrac{1}{2}(-\eta_3 + \eta_4), \qquad \iint q^2\eta_2 dx \quad = -\tfrac{1}{2}\eta_1, \quad . \quad . \quad (9)$$

$$\int q\eta_3 dx \quad = \tfrac{1}{2}(\eta_1 + \eta_2), \qquad \iint q^2\eta_3 dx \quad = \tfrac{1}{2}\eta_4, \quad . \quad . \quad . \quad (10)$$

$$\int q\eta_4 dx \quad = \tfrac{1}{2}(-\eta_1 + \eta_2), \qquad \iint q^2\eta_4 dx \quad = -\tfrac{1}{2}\eta_3, \quad . \quad . \quad (11)$$

$$\int q(\eta_3 - \eta_4)dx = \eta_1, \qquad \iint q^2(\eta_3 - \eta_4) = \tfrac{1}{2}(\eta_3 + \eta_4), \quad . \quad (12)$$

$$\int 2q^2 x\eta \, dx \quad = B_2 lq(-\eta_3 + \eta_4) + B_2(\eta_1 - 1) + 2B_3 lq\eta_1 - B_3(\eta_3 + \eta_4), \quad (13)$$

$$\eta_1 = \operatorname{ch} ql \cos ql, \quad \eta_2 = \operatorname{sh} ql \sin ql, \quad \eta_3 = \operatorname{sh} ql \cos ql, \quad \eta_4 = \operatorname{ch} ql \sin ql, \quad (14)$$

$$\frac{2q^2}{B_3}\int_0^l x\eta \, dx = (-lq \operatorname{sh} ql \cos ql + lq \operatorname{ch} ql \sin ql + \operatorname{ch} ql \cos ql - 1)(\operatorname{th} ql + \tan ql)$$

$$+ 2lq \operatorname{ch} ql \cos ql - \operatorname{sh} ql \cos ql - \operatorname{ch} ql \sin ql$$

$$= lq\frac{\operatorname{ch} ql}{\cos ql} + lq\frac{\cos ql}{\operatorname{ch} ql} - \operatorname{th} ql - \tan ql, \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\frac{2Plq^2}{\rho b B_3} = \frac{2q^2}{B_3}\int x\eta \, dx + \frac{1}{3}ke^3q^4\frac{B_2}{B_3} = lq\left(\frac{\operatorname{ch} ql}{\cos ql} + \frac{\cos ql}{\operatorname{ch} ql}\right), \quad \frac{1}{3}ke^3q^4 = 1, \quad (16)$$

and if d is the deflexion at the free end,

$$\frac{d}{B_3} = \frac{B_2}{B_3}\eta_2 + \eta_3 - \eta_4 = (\operatorname{th} ql + \tan ql)\operatorname{sh} ql \sin ql$$
$$+ \operatorname{sh} ql \cos ql - \operatorname{ch} ql \sin ql$$

$$= \frac{\operatorname{sh} ql}{\cos ql} - \frac{\sin ql}{\operatorname{ch} ql} = \frac{\operatorname{sh} 2ql - \sin 2ql}{2 \operatorname{ch} ql \cos ql}, \quad \cdots \quad (17)$$

$$d = \frac{Pq}{\rho b} \cdot \frac{\operatorname{sh} 2ql - \sin 2ql}{\operatorname{ch}^2 ql + \cos^2 ql} \cdot \quad \cdots \quad (18)$$

This reduces to the preceding value of d in (4) § 8 when ql is small, and the buoyancy is neglected.

Velocity of Sound in Air.

15. The question of sound velocity may receive reconsideration here.

For the velocity W of longitudinal vibration through ice or a solid substance, we have taken

$$W^2 = g\frac{E}{\rho} = gk, \quad \cdots \quad (1)$$

so that the velocity is that acquired in falling freely under gravity through half the elastic length.

But in air the cubical elasticity, $\rho\frac{dp}{d\rho}$, which on Boyle's isothermal law is equal to the pressure, becomes γ times the pressure in the adiabatic compression and expansion of rapid vibration; so that the velocity of sound in air is taken as the velocity acquired in falling through γ times half the height of the homogeneous atmosphere; and this γ is the ratio of the specific heat (S.H.) at constant pressure and constant volume, taken on the average at $\gamma = 1\cdot4$.

Suppose, however, a shower of rain is falling : how does this affect the value of γ, and the velocity of sound ?

The thermodynamical influence is the same as that investigated by Sir Andrew Noble in his " Research on the Pressure and Work of fired Gunpowder," Phil. Trans. 1875–94.

There he found by his experiments on the pressure in a closed vessel, that the law connecting pressure with volume and density was something intermediate to the isothermal law, with $\gamma = 1$, and the adiabatic law, $\gamma = 1\cdot4$; and he accounted for the difference by the influence of the heat stored up in the solid particles of powder in the gas.

Take a pound of gunpowder, and explode it in a closed steel vessel of volume C inches³; and suppose the fraction β lb was solid and non-gaseous, leaving $1-\beta$ lb in a state of gas.

In a rise of temperature of dT degrees Fahrenheit (F.) the heat dH, in British Thermal Units (B.T.U.), given out by the non-gaseous part, of S.H. λ, is given by

$$d\text{H} = -\beta\lambda\,d\text{T}. \qquad \cdots \qquad (2)$$

Denoting the volume of the non-gaseous part by α, the gaseous part, $1-\beta$ lb, obeys the gas-equation

$$\frac{p(v-\alpha)}{\text{T}} = \frac{p_0(v_0-\alpha)}{\text{T}_0}, \qquad \cdots \qquad (3)$$

where T, T_0 denote absolute temperature F.; so that, taking logarithmic differentials,

$$\frac{dp}{p} + \frac{dv}{v-\alpha} - \frac{d\text{T}}{\text{T}} = 0 ; \qquad \cdots \qquad (4)$$

and then with (2),

$$\frac{d\text{H}}{\text{T}} = -\beta\lambda\left(\frac{dp}{p} + \frac{dv}{v-\alpha}\right). \qquad \cdots \qquad (5)$$

Supposing p and v to vary one at a time,

$$d\text{H} = \frac{\partial \text{H}}{\partial p}\,dp\ (v\text{ constant}) + \frac{\partial \text{H}}{\partial v}\,dv\ (p\text{ constant}), \quad (6)$$

where, when p varies while v is constant,

$$\frac{\partial \text{H}}{\partial p} = \frac{\partial \text{H}}{\partial \text{T}}\frac{\partial \text{T}}{\partial p} = (1-\beta)\text{C}_v\frac{v-\alpha}{\text{R}} = (1-\beta)\text{C}_v\frac{\text{T}}{p}, \quad (7)$$

and when p is constant and v varies, for $1-\beta$ lb of gas,

$$\frac{\partial \text{H}}{\partial v} = \frac{\partial \text{H}}{\partial \text{T}}\frac{\partial \text{T}}{\partial v} = (1-\beta)\text{C}_p\frac{p}{\text{R}} = (1-\beta)\text{C}_p\frac{\text{T}}{v-\alpha}, \quad (8)$$

C_v, C_p denoting the S.H. of the one lb of gaseous product at constant volume and constant pressure; so that (6) becomes

$$\frac{d\text{H}}{\text{T}} = (1-\beta)\text{C}_v\frac{dp}{p} + (1-\beta)\text{C}_p\frac{dv}{v-\alpha}. \qquad (9)$$

Equating these values in (5) and (9),

$$\left[(1-\beta)C_v + \beta\lambda\right]\frac{dp}{p} + \left[(1-\beta)C_p + \beta\lambda\right]\frac{dv}{v-\alpha} = 0, \quad . \quad (10)$$

a differential relation, leading on integration to

$$\left[(1-\beta)C_v + \beta\lambda\right]\log p + \left[(1-\beta)C_p + \beta\lambda\right]\log(v-\alpha)$$
$$= \text{a constant,} \quad . \quad . \quad . \quad (11)$$

$$\frac{p}{p_0} = \left(\frac{v_0-\alpha}{v-\alpha}\right)^m, \quad m = \frac{(1-\beta)C_p + \beta\lambda}{(1-\beta)C_v + \beta\lambda}, \quad . \quad . \quad (12)$$

reducing to the ordinary adiabatic equation when $\alpha, \beta = 0$.

In the experiments of Noble and Abel, they found

$$\frac{\alpha}{v_0} = 0{\cdot}57, \quad \frac{v_0-\alpha}{v_0} = 0{\cdot}43, \quad \frac{\beta}{1-\beta} = \frac{\alpha}{v_0-\alpha} = 1{\cdot}3256, \quad (13)$$

taking the solid and gaseous products of the same density when fired;

$$\lambda = 0{\cdot}45, \quad C_p = 0{\cdot}2324, \quad C_v = 0{\cdot}1762, \quad . \quad (14)$$

making

$$m = 1{\cdot}074, \quad \text{against} \quad \gamma = \frac{C_p}{C_v} = 1{\cdot}33. \quad . \quad . \quad (15)$$

Thus 57 per cent of this gunpowder would issue as smoke from the muzzle of a gun. But with modern powder, such as cordite, the solid part of explosion or smoke is insensible, and the index m regains the full value of γ.

The raindrops in the air are the equivalent of the non-gaseous part of the powder gas, and their effect is to reduce the value of γ, and diminish the velocity of sound.

16. Next treat the air in an unsaturated state as a mechanical mixture of dry air and aqueous vapour, each obeying the laws of the Gas Equation.

The question has been considered by Professor C. Niven for a mixture of any number of gases, and he gives the formula (Solutions of the Senate House Problems, 1878, p. 66)

$$U^2 = \frac{\Sigma\, mk}{\Sigma\, mc}\frac{\Sigma\dfrac{mc}{k}\,u^2}{\Sigma\, m} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for U the sound-velocity in the mixture, where m denotes the density of a gas, c the S.H. at constant volume, k at constant pressure, and u the velocity of sound in that gas.

Take a cubic centimetre of the mixture of m_1 grams of dry air and m_2 of aqueous vapour; and let heat be supplied to raise the temperature $\delta\theta$ degrees, without change of volume; denoting by C the S.H. of the mixture at constant volume,

$$(m_1 + m_2)\, \text{C}\, \delta\theta = m_1 c_1 \delta\theta + m_2 c_2 \delta\theta, \quad \text{C} = \frac{m_1 c_1 + m_2 c_2}{m_1 + m_2}; \quad (2)$$

and similarly, if K denotes the S.H. at constant pressure,

$$\text{K} = \frac{m_1 k_1 + m_2 k_2}{m_1 + m_2}. \quad \cdots \cdots \quad (3)$$

Also for each constituent gas respectively, with gravitation measure of the pressure,

$$u_1^2 = g\gamma_1 h_1 = g\frac{k_1}{c_1}\frac{p_1}{m_1}, \quad p_1 = \frac{m_1 c_1}{k_1}\frac{u_1^2}{g}, \quad p_2 = \frac{m_2 c_2}{k_2}\frac{u_2^2}{g}, \quad (4)$$

and for the mixture,

$$\text{P} = \frac{(m_1 + m_2)\text{C}}{\text{K}}\frac{\text{U}^2}{g} = p_1 + p_2, \quad \cdots \cdots \quad (5)$$

$$\frac{\text{U}^2}{g} = \frac{\text{K}}{\text{C}}\frac{p_1 + p_2}{m_1 + m_2} = \frac{m_1 k_1 + m_2 k_2}{m_1 c_1 + m_2 c_2}\frac{\dfrac{m_1 c_1}{k_1}\dfrac{u_1^2}{g} + \dfrac{m_2 c_2}{k_2}\dfrac{u_2^2}{g}}{m_1 + m_2}, \quad (6)$$

the special case for two gases of Niven's general formula, derived in the same way.

The Smithsonian Tables will provide the numerical data from which U can be given in a tabular form from p, m, c, k of dry air, and aqueous vapour of given saturation.

1 Staple Inn, W.C.
  Oct. 1915.

II. *A Criticism on van der Waals' Equation and some New Equations derived therefrom.* By JAMES KAM[*].

Preface.

IN the following deductions I take it for granted that the factors a and b of van der Waals' equation have the effect:

The factor a of diminishing the gas-pressure towards the exterior with a value $\text{P}_1 = \dfrac{a}{\text{V}^2}$, the "Inward Pressure";

The factor b of increasing that pressure at the rate $\dfrac{\text{V}}{\text{V}-b}.$

Thus the pressure P from the exterior on the gas plus the "Inward Pressure" P_1 is the total pressure Π, *i. e.*,

$$P + P_1 = \Pi.$$

It will be seen that I introduce two separate factors b and β, the latter of which is used in place of van der Waals' factor b.

b is the volume of N molecules filling a volume $\phi = (V + b)$, at a pressure $\Pi = \dfrac{R \cdot T}{V}$.

β is the volume of N_1 molecules filling the volume V at the same temperature and pressure. Consequently b is a constant, β a variable ; for the smaller V is (*i. e.* the greater the compression) the less the number of molecules required to exert a pressure $\Pi = \dfrac{R \cdot T}{V}$.

Hence the inverse value of the volume V at any pressure $\Pi = \dfrac{R \cdot T}{V}$ is not the density $\dfrac{1}{V}$, but the density $\dfrac{1}{(V + b)}$, which as b is a constant increases less rapidly than the volume V decreases.

For large values of V (*i. e.* small value of Π), V will be almost equal to $\phi = (V + b)$, N_1 almost equal to N, and β almost equal to b.

For small values of V these factors deviate considerably.

Introduction.

I.

According to van der Waals, the "Inward Pressure" P_1 supports the pressure P from the exterior, and the total pressure a gas thus bears is

$$\Pi = P + P_1 = \frac{R \cdot T}{V - b},$$

or considering $P_1 = \dfrac{a}{V^2}$,

$$P + \frac{a}{V^2} = \frac{R \cdot T}{V - b}.$$

Evidently Π is made equal to the pressure of a "perfect" gas of the same temperature at the volume $(V - b)$.

In the above equation

$$R = \frac{P_0 . V_0}{273} ;$$

whereas it will be remembered

$$P_0 = \frac{1}{3} N . m . c^2 ;$$

N being the number of molecules per unit of volume, m the mass of a molecule, c the velocity of mean square. The molecules themselves are considered to be mathematical points, and b (the volume of N molecules) here consequently is zero.

In reality b has a positive and definite value and increases the number of impacts, or the pressure, at the rate $\frac{V}{V-b}$, as was shown by van der Waals.

An actual gas consequently exercises the same pressure P_0 at a greater volume ; *i. e.* the *same* volume V_0 contains less molecules, say only N_1, having a volume β, smaller than b.

Per unit of volume we thus get a decrease of impacts, caused by the decrease of the number of molecules at the rate $\frac{N_1}{N}$, and an increase of impacts at the rate $\frac{V_0}{V_0-\beta}$, caused by the influence of β, and the effect of the former is compensated by the latter.

It is evident that the greater the compression, the smaller the number of molecules per unit of volume of an actual gas as compared with a perfect gas of the same pressure and temperature.

We may call $\frac{N_1}{N}$ the specific density of a gas ; its value is greatest when the density is smallest, but always smaller than 1 ; it decreases in value as the compression proceeds.

This circumstance not being fully considered by van der Waals' equation, causes large deviations.

II.

If at the volume V and temperature T, N molecules of a " perfect " gas exert a pressure

$$\Pi = \frac{R . T}{V},$$

then N molecules of an actual gas would exert this pressure at a volume $\phi = (V + b)$ and the same temperature, b being the volume of these N molecules.

The volume V would contain of the latter

$$N_1 = \frac{V}{V+b} N \text{ molecules,} \quad \cdots \quad (1)$$

having a volume

$$\beta = \frac{V}{V+b} b. \quad \cdots \quad \cdots \quad (2)$$

The specific density referred to in the introduction is

$$\nu = \frac{N_1}{N} = \frac{V}{V+b}, \quad \cdots \quad \cdots \quad (3)$$

and expresses the density of an actual gas with regard to a perfect gas at the same temperature and pressure Π.

For the perfect gas,

$$\Pi = \frac{R \cdot T}{V} ;$$

and for the actual gas at the same volume V,

$$\Pi = \frac{\nu \cdot R \cdot T}{V - \beta}. \quad \cdots \quad \cdots \quad (4)$$

As stated above, we must of course find

$$\frac{\nu \cdot R \cdot T}{V - \beta} = \frac{\frac{V}{V+b} \cdot R \cdot T}{V - \frac{V}{V+b} \cdot b} = \frac{R \cdot T}{V}.$$

On the other hand we had

$$\Pi = P + P_1.$$

P_1, the inward pressure, being inversely proportional to the density, *i. e.* to $\frac{1}{V+b}$, is equal to $\frac{a}{(V+b)^2}$ if a is the constant at $V=1$; and instead of van der Waals' equation, we find

$$P + \frac{a}{(V+b)^2} = \frac{R \cdot T}{V} \cdots \quad \cdots \quad (A)$$

In this equation b, the volume of N molecules, is naturally constant. The equation expresses that at the density $\frac{1}{V+b}$ and the volume V, an actual gas exerts the same pressure Π as a perfect gas at the density $\frac{1}{V}$ and the same temperature.

Making $c = \nu^2 a$, we could write equation (A) in the form

$$P + \frac{c}{V^2} = \frac{\nu \cdot R \cdot T}{V - \beta}, \quad . \quad . \quad . \quad . \quad (B)$$

in which equation ν and β have the values given by (1) and (2) and thus are variables.

Equation (B) naturally leads to the equation

$$P + \frac{c}{V^2} = \frac{R \cdot T}{V}, \quad . \quad . \quad . \quad . \quad (C)$$

a quadratic equation to be discussed later on.

Equations (A) and (B) are cubic equations in V, having three roots. With regard to the volume they thus are of the third degree.

With regard to the density, however, they are of the second degree, the density at the pressure $\frac{R \cdot T}{V}$ being $\frac{1}{V + b}$.

Thus in equation (A), V on the left only applies to the volume, on the right to volume and inverse density, and the meaning is not entirely identical, and we could not write it in the form (making $\phi = (V + b)$)

$$P + \frac{a}{\phi^2} = \frac{R \cdot T}{\phi - b},$$

as here we would have an equation of the third degree of the density, instead of the quadratic which (A) is.

Neither could we write (A) in the form

$$P + \frac{a}{V^2} = \frac{R \cdot T}{V - b},$$

as the volume of the molecules contained by V is not b but only β, which is a variable (*vide* equation 2).

Still we can consider (A) of the third degree of V, the volume, and its curve thus as cutting a horizontal pressure-line in three points, denoting the three values of V. The two points of the curve for which $\frac{dp}{dv} = 0$ approach more towards each other as the temperature rises, till at the critical point they coincide.

For this point we then have

$$\frac{dp}{dv} = 0, \qquad \frac{2a}{(V_c + b)^3} = \frac{R \cdot T_c}{V_c^2},$$

$$\frac{d^2p}{dv^2} = 0, \qquad \frac{6a}{(V_c + b)^4} = \frac{2 \cdot R \cdot T_c}{V_c^3}$$

whence we obtain

$$V_c = 2b. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

b here is the volume of N molecules exerting the same pressure at the volume $(V_c + b)$ as N molecules of a perfect gas at the volume V_c (which of the actual gas only contains N_1 molecules).

In accordance with (1) we find for N_1

$$N_1 = \nu \cdot N = \frac{V_c}{V_c + b} \cdot N = \frac{2}{3} N, \\ \text{and} \quad \nu = \frac{N_1}{N} = \frac{2}{3}, \qquad \left. \right\} \quad . \quad . \quad . \quad (6)$$

and the volume of these N_1 molecules is

$$\beta = \frac{V_c}{V_c + b} \cdot b = \frac{2}{3} b. \quad . \quad . \quad . \quad . \quad (7)$$

(5) and (7) give

$$V_c = 2b = 3\beta. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Substituting ν and β in equation (4) we find

$$\Pi = \frac{\nu \cdot R \cdot T_c}{V_c - \beta} = \frac{\frac{2}{3} \cdot R \cdot T_c}{2b - \frac{2}{3} b} = \frac{R \cdot T_c}{2b} = \frac{R \cdot T_c}{V_c}.$$

From (6) we deduce that the density at the critical state is *for all substances* $\frac{2}{3}$ of the theoretical one, or $\frac{2}{3}$ of the density of a perfect gas exerting at the same volume a pressure equal to the critical pressure at the critical temperature.

This in combination with (8) may well lead us to suppose that the gaseous laws again hold good for the critical state. We shall see presently that this actually is the case.

In an entirely similar manner we deduce from (B)

$$\frac{dp}{dv} = 0, \qquad \frac{2c}{V_c^3} = \frac{\nu \cdot R \cdot T_c}{(V_c - \beta)^2},$$

$$\frac{d^2p}{dv^2} = 0, \qquad \frac{6c}{V_c^4} = \frac{2\nu \cdot R \cdot T_c}{(V_c - \beta)^3},$$

whence $\qquad\qquad V_c = 3\beta, \quad . \quad . \quad . \quad . \quad . \quad (8a)$

a value in accordance with (8).

We have already seen that equation (A) is not identical with van der Waals' equation.

It will also be seen that the usual solution of the latter by multiplying and arranging according to powers of V_c cannot afford correct values of P_c and P_{1c}. For doing so, we consider $\frac{1}{V_c}$ the density (or the pressure) to be the inverse value of V (the volume) which for an actual gas can never be, so long as b has a positive and definite value.

Where the values

$$3V_c{}^2 = \frac{a}{P_c} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (a)$$

and

$$V_c{}^3 = \frac{a \cdot b}{P_c}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (b)$$

and consequently $V_c = 3b$ are found, a and P_c divide out, and the density does not affect the result (as b here has the meaning of β in equations (2), (4) and (B)).

The expression

$$P_c = \frac{a}{3V_c{}^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (c)$$

resulting from (a), however, cannot be correct, and the same consequently applies to

$$P_{1c} = \frac{a}{V_c{}^2} = 3P_c,$$

resulting from (c).

Hence the values

$$\Pi_c = P_c + P_{1c} = 4P_c = \frac{4a}{3V_c{}^2}$$

and

$$\Pi_c = \frac{R \cdot T_c}{V_c - b} = \frac{R \cdot T_c}{2b} = \frac{3}{2} \frac{R \cdot T_c}{V_c},$$

which result from this solution of the equation of van der Waals, do **not** correspond as they should do. For the correction-factors $\frac{a}{V^2}$ and b should cause the same increase of pressure on either side of the equation.

On substitution of $V_c = 2b$ in equation (A) (or of $V_c = 3\beta$ in (B)), we obtain a quadratic equation.

Multiplying and arranging according to powers of b, we find for the critical state

$$b^2 - \frac{R \cdot T_c}{P_c} \cdot b + \frac{a}{9P_c} = 0, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (D)$$

and thus $\quad b = \frac{R \cdot T_c}{4P_c} \pm \sqrt{\left\{ \frac{R \cdot T_c}{4P_c} \right\}^2 - \frac{a}{9P_c}}.$

There is, however, only one value of b. Hence

$$b = \frac{R \cdot T_c}{4P_c}, \quad \text{and} \quad \left\{ \frac{R \cdot T_c}{4P_c} \right\}^2 = \frac{a}{9P_c},$$

or

$$b^2 = \frac{a}{9P_c},$$

and thus

$$P_c = \frac{R \cdot T_c}{2 V_c}, \quad \text{or} \quad 2 P_c \cdot V_c = R \cdot T_c, \quad . \quad . \quad . \quad (9)$$

and

$$P_c = \frac{a}{9 b^2} = \frac{a}{(V_c + b)^2} = P_{1c}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

As $P_c = P_{1c}$, we can write (9) $2 P_{1c} \cdot V_c = R \cdot T_c$.

$$\Pi_c \cdot V_c = R \cdot T_c, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which is the " gaseous law " for the critical state.

Equation (10) shows that critical " Inward Pressure " and critical pressure are equal, a deduction obtainable in an entirely different and independent manner, as will be shown later on.

We will, however, first introduce yet another correction which, together with the preceding ones, leads up to interesting results.

III.

Another factor influencing the number of molecules per unit of volume is the temperature.

In equations (A), (B) and (C) we consider V as a fraction of the original volume at the temperature T.

If, however, V is given as a fraction of V_0, *i. e.* of the volume reduced to $0°$ C. and 760 mm. pressure, it is necessary to introduce yet one other correction.

At the temperature T and pressure $P_0 = \frac{R \cdot T}{V}$ the number of molecules contained by V_0 is

$$\epsilon = \frac{N}{T} \cdot 273 \text{ (molecules of a perfect gas).}$$

Hence the factor of specific density ν has to be corrected in the same manner, and we obtain for equation (A)

$$P + \frac{a}{(V + b)^2} = \frac{\nu \cdot \dfrac{273}{T} \cdot R \cdot T}{V - \beta},$$

or

$$P + \frac{a}{(V + b)^2} = \frac{1}{V}; \quad . \quad . \quad . \quad . \quad . \quad (A_1)$$

and instead of (C) we obtain

$$P + \frac{c}{V^2} = \frac{1}{V}. \quad . \quad . \quad . \quad . \quad . \quad (C_1)$$

At the critical state $V_c = 2b$ and (A) becomes

$$P_c + \frac{a}{9b^2} = \frac{1}{2b},$$

a quadratic equation, really a special form of $(C_1 j)$. Writing it in the form

$$b^2 - \frac{1}{2P_c} b + \frac{a}{9P_c} = 0,$$

we find

$$b = \frac{1}{4P_c} \pm \sqrt{\left\{\frac{1}{4P_c}\right\}^2 - \frac{a}{9P_c}};$$

and as b naturally has only one value,

$$b = \frac{1}{4P_c} \quad \text{and} \quad \left\{\frac{1}{4P_c}\right\}^2 - \frac{a}{9P_c} = 0,$$

or

$$b^2 = \frac{a}{9P_c}.$$

We thus get the two values

$$P_c = \frac{1}{2V_c} \quad \text{or} \quad 2P_c V_c = 1 = \text{constant}, \quad . (12)$$

and

$$P_c = \frac{a}{9b^2} = \frac{a}{(V_c + b)^2} = P_{1c}. \quad . . . . . (13)$$

The accuracy of equation (12) is demonstrated by the figures of the table on the next page, taken from "Landolt-Börnstein," *Physikalische Tabellen*, Berlin, 1905, pp. 181–186 The values marked * are borrowed from *Handbuch der Physik*, A. Winkelmann, vol. iii. Leipzig 1906, pp. 859–868.

Equation (12),

$$2P_c . V_c = 1 \text{ (constant)}$$

or

$$\Pi_c . V_c = 1 \text{ (constant)},$$

Π being the total pressure a gas bears, shows the interesting fact that the law of Boyle-Mariotte is true again for the critical state.

Naturally, if during the course of the experiment molecules have either dissociated or condensed, we must find deviation over and above such as caused by the errors of observation made in determining P_c and V_c.

At the critical state, small changes of pressure cause large

changes of volume. I therefore selected all data of experiments affording corresponding values of V_c and P_c, as will be noticed. Values of V_c and P_c determined independently cannot be trusted to give reliable proof.

	V_c.	P_c (exp.).	P (calc.).
Acetic acid	·0066	57·11	75·7
Alcohol	·00713	62·76	70
Amyl formate	·01710	34·12	29·2
Benzene	·00981	47·9	50·9*
Benzene chloride	·01175	44·62	42·5*
Ether	·01334	37·5	37·8
Ethyl acetate	·01222	39·65	41
Ethyl butyrate	·01744	30·24	28·80
Ethylene dichloride	·00982	53	51
Ethyl isobutyrate.................	·01749	30·13	28·6*
Ethyl propionate	·01482	33·86	33·75
Isobutyl acetate	·01717	31·4	29·41
Isobutyl formate	·01472	38·29	37·86
Methyl acetate	·0096	47·54	52
Methyl butyrate	·01455	36·02	34·4
Methyl ethyl ether	·00873	46·27	57
Methyl propionate	·01224	39·88	40·8
Methyl valerate	·01728	31·5	29
Propyl acetate	·01464	34·8	34·5
Propyl alcohol	·00968	50·16	51·3
Propyl chloride	·00982	49	50·9*
Propyl formate....................	·01203	42·7	41·5
H_2O.	·003864	194·61	130
N_2O	·00436	77·5	114
SO_2	·00587	78·9	85
CO_2	·0066	77	76
CS_2	·009011	72·868	60

We can, of course, also derive the same result[*] from equation (C_1).

For the critical state we have, multiplied and arranged :

$$V_c{}^2 - \frac{1}{P_c} V_c + \frac{c}{P_c} = 0,$$

$$V_c = \frac{1}{2P_c} \pm \sqrt{\frac{1}{4P_c{}^2} - \frac{c}{P_c}}.$$

At the critical state V_c adopts only one value. Hence

$$V_c = \frac{1}{2P_c}, \qquad V_c{}^2 = \frac{c}{P_c},$$

or

$$P_c = \frac{1}{2V_c}, \quad \text{and} \quad P_c = \frac{c}{V_c{}^2} = P_{1c}.$$

We here find the same values as found in (12) and (13)

$$\left(c = v^2 \cdot a = \left(\frac{V_c}{V_c + b}\right)^2 a. \quad \text{See equations A \& B, pp. 25, 26.}\right)$$

Apart from being a point of the critical isothermal, the critical point thus appears to belong as well to two other curves of the equations :

$$2P_c \cdot V_c = 1 \text{ (constant)},$$

and

$$P + \frac{c}{V^2} = \frac{1}{V}.$$

The latter curve cuts a horizontal equal pressure-line twice, denoting the two values of V satisfying the equation. At the vertex of the curve for which $\frac{dp}{dv} = 0$ and the two values of V become equal, we have the critical point. Thus we would find for the critical point, $\frac{dp}{dv} = 0$:

$$\frac{2c}{V_c^3} = \frac{1}{V_c^2},$$

or

$$c = \frac{V_c}{2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (14)$$

which value substituted in the original equation gives us
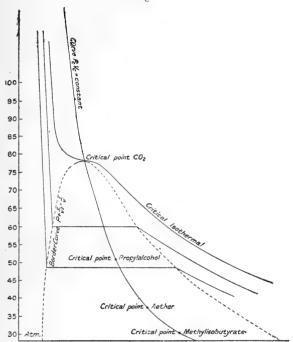
$$P_c + \frac{1}{2V_c} = \frac{1}{V_c},$$

or

$$P_c = \frac{1}{2V_c}, \quad 2P_cV_c = 1 \text{ (constant)},$$

and

$$P_c = \frac{c}{V_c^2} = P_{1c},$$

in accordance with (12) and (13).

It will be seen that the curve satisfying equation (C_1) is formed by the line drawn through the points where the isothermals below the critical temperature change into and from the horizontal straight line, and which is known as the "border-curve." As the temperature approaches the critical temperature, the horizontal straight line gets shorter and shorter and the two volumes converge more and more towards the same value, *i. e.* the critical volume, which is reached at the vertex of the border line.

The diagram roughly shows that the critical point is the point of intersection of three curves, *i. e.* the critical isothermal, the border-curve, and the curve

$$2P_c \cdot V_c = 1 \text{ (constant)}.$$

Fig. 1.

We found equation (14) $c = \dfrac{V_c}{2}$. Considering $c = \nu^2 \, a$

(p. 26, equation B) and $\nu = \dfrac{V_c}{V_c + b}$, we find, as $V_c = 2b$,

$\dfrac{4}{9} a = b$, and

$$a = \frac{9}{4} b = \frac{9}{8} V_c. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

We can deduce the same value from equation (A), p. 25, for the critical state.

As we found

$$P_c = P_{1c} = \frac{a}{(V_c + b)^2},$$

we get

$$\frac{2a}{(V_c + b)^2} = \frac{1}{V_c},$$

and as $V_c = 2b$,

$$\frac{2a}{9b^2} = \frac{1}{2b};$$

whence

$$a = \frac{9}{4}b = \frac{9}{8}V_c,$$

as found in (15).

Substituting V_c in equation (A), $V_c = 2b$, we obtain

$$\frac{2a}{9b^2} = \frac{R \cdot T_c}{2b},$$

whence

$$T_c = \frac{4a}{9b \cdot R}. \quad \cdots \quad \cdots \quad (16)$$

As $b = \frac{3}{2}\beta$ (equation (8), p. 27),

$$T_c = \frac{8}{27} \cdot \frac{a}{\beta \cdot R}, \quad \cdots \quad \cdots \quad (17)$$

which is the identical form for the critical temperature as found by van der Waals.

Equation (9) p. 29, gives for T_c the value

$$T_c = \frac{2 \cdot P_c \cdot V_c}{R}, \quad \cdots \quad \cdots \quad (18)$$

and as $V_c = 3\beta$, we find in combination with (17)

$$\frac{6P_c \cdot \beta}{R} = \frac{8}{27} \cdot \frac{a}{\beta \cdot R},$$

or

$$P_c = \frac{4a}{81\beta^2}, \quad \text{or as } \beta = \frac{2}{3}b,$$

$$P_c = \frac{a}{9b^2} = \frac{a}{(V_c + b)^2} = P_{1c},$$

in accordance with the preceding.

It may be of interest to compare the above with an experiment.

In the case of carbonic acid, Andrews found for V_c and P_c:

$$V_c = {\cdot}0066,$$
$$P_c = 77 \text{ atmospheres.}$$

We have, equation (15), p. 33,

$$a = \frac{9}{8}V_c = {\cdot}007425,$$

and equation (8), p. 27,

$$b = \frac{1}{2}V_c = {\cdot}0033.$$

Hence according to equation (10), p. 29,

$$P_c = \frac{a}{(V_c + b)^2} = \frac{\cdot 007425}{9 \cdot (\cdot 0033)^2} = 76 \text{ atmospheres,}$$

which is the same value calculated according to equation (12), p. 30, as shown by table, p. 31, and very nearly the pressure found by Andrews.

For methyl acetate, $V_c = \cdot 0096$, $P_c = 47 \cdot 54$, we find in the same manner $P_c = 52\ 08$.

For propyl alcohol, $V_c = \cdot 0098$, $P_c = 50 \cdot 16$, we find $P_c = 51 \cdot 65$, and so on.

For T_c, according to equation (16) or (17), we find for carbonic acid, $T_c = 273°$, as should be, considering the value of $V_c = \cdot 0066$ is the volume relative to the original volume reduced to $0°$ and 760 mm.

The constant a for carbonic acid calculated above has a somewhat smaller value than the one van der Waals finds $(a = \cdot 00874)$.

The value van der Waals calculates for P_c is (for CO_2) 61 atmospheres.

IV.

On a future occasion we will show that the equality of P_c and P_{1c} can be proved in an entirely different and independent manner.

A natural consequence of this equality would be the disappearance of the phenomena of surface-tension and of the latent heat of vaporization at the critical point. For the cohesive forces would be compensated by the thermic pressure, and the transference of a molecule from the interior of the fluid to the space over its surface would not require any work against a force.

But we cannot imagine $P_c = P_{1c}$, and still measure an actual critical pressure P_c towards the exterior, unless we assume the law of equality of action and reaction to apply to the cohesive forces, as to all other forces. Thus the surface molecules, attracted by the interior molecules, must exert the same attraction on the latter, equally strong but opposite in direction.

Between the surface and the interior the thermic pressure would be supported by the cohesive forces, the density would be greatest at the surface and gradually diminish towards the interior.

If Π were the pressure without any molecular attraction throughout the fluid, then the pressure from the interior
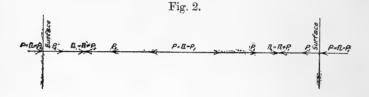
would be supported towards the surface and diminished in the opposite direction, with the value of the attraction P_1, if there were any such attraction,—*i. e.* the pressure in the surface-layer would become $\Pi_1 = \Pi + P_1$, and the pressure at the surface and in the interior would become

$$P = \Pi - P_1,$$

as illustrated by our diagram (fig. 2). In particular, if $P_c = P_{1_c}$ we should thus have

$$\Pi = P_c + P_{1c} = 2P_c = 2P_{1c},$$

or

$$P_c = P_{1c} = \tfrac{1}{2}\Pi.$$

Fig. 2.

No matter how great P_1, the pressure in the interior must be transmitted undiminished towards the surface. But the pressure between surface and interior is increased and attains at the critical state (thus for $P_c = P_{1c}$) a value

$$\Pi_1 = \Pi + P_{1c} = 3P_c.$$

The force opposing Π_1 is identical with the "Intrinsic pressure" of Laplace in the case of liquids.

Instead of causing an increase of pressure in the interior, the cohesive forces are the means of such increase *between* surface and interior equal to their numerical value, and of a decrease of pressure in the interior of that equivalent. This, however, does not affect our equations (A) and the following. For the gas-pressure P is equal to the pressure Π the gas would exert if there were no molecular attraction, minus the value of that attraction P_1, *i. e.*,

$$P = \Pi - P_1,$$

or

$$P + \frac{a}{(V+b)^2} = \frac{R \cdot T}{V}.$$

Additional evidence in support of this view will be brought forward on a future occasion.

III. *On the Variation of Surface-Tension with Temperature.*
By ALLAN FERGUSON, *D.Sc.(Lond.), Assistant-Lecturer
in Physics, in the University College of North Wales,
Bangor* *.

OVER ranges of, say, twenty or thirty degrees the effect
of temperature on surface-tension can be expressed
with considerable accuracy by a linear formula of the type

$$T = T_0(1 - \alpha\theta). \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

For wider ranges such a formula cannot be used with
even approximate accuracy, and formulæ of the type

$$T = T_0(1 - \alpha\theta \pm \beta\theta^2) \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

have been used to represent the experimental facts. Such
formulæ, however, will not bear extrapolation over even a
moderate range of temperature, and if, in particular, they
be applied to estimate the critical temperature by calculating
the value of θ for which T vanishes, they invariably give
wildly discordant values for θ_c.

The directly determined values for the critical tempera-
tures of liquids are comparatively few in number, and it is
a matter of some importance to be able to estimate the critical
temperature of a liquid to within a degree or two; for,
amongst other things, the problem of tracing relations
between surface-tension and chemical constitution has been
considerably obscured by a habit of making comparisons at
the same temperatures. Schiff † recognized that better
results were to be obtained by making comparisons at
" corresponding temperatures," and chose the boiling-point
at atmospheric pressure for the purpose of comparison.
This, of course, implies that the ratio of the boiling-point to
the critical temperature is a constant for all liquids when
temperatures are measured on the absolute scale, and, as I
have shown in a recent paper ‡, this is by no means exactly
true, as the ratio is markedly affected by constitutive
influences.

It is very necessary, therefore, to have some means of
estimating the critical temperature of a liquid with fair
accuracy, and, as will be shown later, this estimate may be

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* Communicated by Prof. E. Taylor Jones.
† Liebig's *Ann.* ccxliii. p. 47 (1884).
‡ Phil. Mag. April 1915, p. 599.

made (for unassociated liquids) by observations of the tem-
perature-variation of surface-tension over a comparatively
limited range.

Some little time ago I pointed out that the equation

$$T = T_0(1 - b\theta)^n \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

represented the surface-tension of benzene with considerable
accuracy between $0°$ and the critical temperature[*]. Such a
formula, if of wide application, would be very valuable, as,
in addition to its use in obtaining the surface-tension of a
liquid at any temperature over a wide range, it gives the
critical temperature at once from the equation

$$\theta_c = \frac{1}{b}, \quad . \quad . \quad . \quad . \quad . \quad \text{(iv.)}$$

and so enables us to make a comparison of surface-tensions
at any desired corresponding temperatures.

There are very few formulæ which represent the effect of
temperature on surface-tension over any wide range, but I
have recently noticed that Van der Waals[†] has put forward
a binomial expression

$$T_m = A\theta_c^{\frac{1}{3}} p_c^{\frac{2}{3}} (1 - m)^B, \quad . \quad . \quad . \quad . \quad \text{(v.)}$$

where m is the "reduced" temperature, and A and B are
constants for all bodies following Eötvös' law. This equation
represents the experimental facts very accurately, but,
demanding as it does a knowledge of the critical data, it is
hardly so suitable for our purposes as (iii.), which is put in
a form which enables one to calculate the critical tempera-
ture from observations of the surface-tension alone. More-
over, as will be seen later, (iii.) fits the experimental data
more accurately than (v.).

The manner in which it was shown that (iii.) represents
the experimental results may be of interest. Differentiating
(iii.) with respect to θ, we have

$$\frac{dT}{d\theta} = -bnT_0(1 - b\theta)^{n-1}, \quad . \quad . \quad . \quad . \quad \text{(vi.)}$$

and therefore

$$T\frac{d\theta}{dT} = -\frac{1 - b\theta}{bn}. \quad . \quad . \quad . \quad . \quad . \quad \text{(vii.)}$$

* Science Progress, Jan. 1915, p. 445.
† *Zeit. für Phys. Chem.* **xiii.** p. 716 (1894).

So that if $T\dfrac{d\theta}{dT}$ be denoted by y, the relation between y and θ is linear. $\dfrac{d\theta}{dT}$ was calculated over ranges of about $20°$ C. by simply taking the differences of θ and dividing by the corresponding differences of T. $T\dfrac{d\theta}{dT}$ was then plotted against θ, and in all the unassociated liquids examined the graph between these quantities was very accurately linear; the values of b and of n were read off directly from the graph.

The following table * shows the results for the fourteen liquids examined.

TABLE I.

(Showing values of b and n in the formula $T = T_0(1 - b\theta)^n$.)

Substance.	n.	b.	$\theta_c = \dfrac{1}{b}$.	θ_c obs.	Diff.
Ether	1·248	·005155	194°	193°·8	+0°·2
Benzene	1·218	·003472	288	288·5	−0·5
Chloro-benzene	1·203	·002793	358	359·2	− 1·2
Carbon tetrachloride ...	1·206	·003553	281·5	283·1	− 1·6
Methyl formate	1·210	·004695	213	214·0	− 1·0
Methyl acetate	1·200	·004274	234	233·7	+0·3
Methyl propionate	1·202	·003891	257	257·4	− 0·4
Methyl butyrate	1·195	·003559	281	281·3	− 0·3
Methyl iso-butyrate	1·228	·003731	268	267·6	+0·4
Ethyl formate	1·187	·004255	235	235·3	− 0·3
Ethyl acetate	1·217	·003984	251	250·1	+0·9
Ethyl propionate	1·192	·003663	273	272·9	+0·1
Propyl formate............	1·231	·003774	265	264·9	+ 0·1
Propyl acetate	1·204	·003623	276	276·2	− 0·2

Mean value of $n = 1·210$.
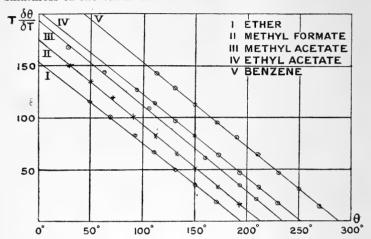
It will be seen from the above table that the critical temperatures are given from the surface-tension data alone with a surprising degree of accuracy. It will also be noticed that n varies very little from liquid to liquid. Its mean value is $1·210$ and, while it is of course preferable to determine n for each liquid separately, this value may be used with some confidence in calculations referring to any other liquid—always provided that it is unassociated—as it happens that, as a simple calculation will show, a small

* The experimental values of T were taken from Ramsay & Shields, Phil. Trans. 1893, p. 647 and Ramsay & Aston, Proc. Roy. Soc. lvi. p. 162 (1894).

variation in n, at moderate temperatures, has not much effect on the computed values of T or of b.

The figure, which is drawn to scale, shows a few of the curves obtained by the process outlined above, and their close approach to parallelism serves further to emphasise the smallness of the variations in n.

The accuracy with which equation (iii.) fits the observed values for the surface-tension is sufficiently shown by Tables II. and III. below. For convenience of comparison the results obtained by the use of Van der Waals' equation (v.) are also given.

TABLE II.

Benzene $\{T = T_0(1 - \cdot003472\,\theta)^{1 \cdot 218}\}$.

		A. F.		V. d. W.	
θ (Cent.).	T obs.	T calc.	Diff.	T calc.	Diff.
0°	...	30·28	...	...	...
80	20·28	20·36	+0·08	20·39	+0·11
100	18·02	18·01	−0·01	18·01	−0·01
120	15·71	15·71	±0·00	15·69	−0·02
140	13·45	13·46	+0·01	13·43	−0·02
160	11·29	11·28	−0·01	11·24	−0·05
180	9·15	9·17	+0·02	9·13	−0·02
200	7·17	7·15	−0·02	7·11	−0·06
220	5·25	5·22	−0·03	5·19	−0·06
240	3·41	3·41	±0·00	3·39	−0·02
260	1·75	1·77	+0·02	1·76	+0·01
280	0·29	0·39	+0·10	0·40	+0·11

TABLE III.

Carbon tetrachloride $\{T = T_0(1 - \cdot003553\,\theta)^{1\cdot206}\}$.

θ (Cent.).	T (obs.).	A. F.		V. d. W.	
		T calc.	Diff.	T calc.	Diff.
0°	...	28·02	...	...	...
20	25·68	25·63	−0·05	25·80	+0·12
80	18·71	18·72	+0 01	18·77	+0·06
100	16·48	16·50	+0·02	16·53	+0·05
120	14·32	14·33	+0·01	14·34	+0·02
140	12·22	12·22	+0·00	12·21	−0·01
160	10·22	10·17	−0·05	10·15	−0·07
180	8·26	8·19	−0·07	8·16	−0·10
200	6·34	6 28	−0·06	6·26	−0·08
220	4·47	4·47	+0·00	4·46	−0·01
240	2·74	2·78	+0·04	2·79	+0·05
260	1·20	1·26	+0·06	1·80	+0·10

The above tables show that, whilst equations (iii.) and (v.) both fit the experimental values very closely, equation (iii.) is distinctly superior in point of accuracy. On the average, the differences between the observed and calculated values given by equation (iii.) are about half those given by equation (v.).

Several attempts have been made to express the critical temperature of a liquid in terms of the temperature coefficient of its surface-tension, perhaps the most widely known being that given by Walden [*]. Assuming a linear law for both T and a^2 $\left(a^2 \equiv \dfrac{2T}{g\rho}\right)$, and writing them in the form

$$T = T_0(1 - \alpha\theta) \quad \text{and} \quad a^2 = a_0^2(1 - K\theta),$$

he finds empirically, from a consideration of the observed values of α, K, and θ_c, that

$$\alpha\theta_c = 1\cdot16 \quad \text{and} \quad K\theta_c = 0\cdot94. \quad . \quad . \quad . \quad \text{(viii.)}$$

As a matter of fact 1·16 and 0 94 are the means of rather variable numbers, and the values of θ_c given by these equations are not very close to the true values, although the mean of the two values given by equations (viii.) is usually better than either value taken separately. Table IV. below, which gives the data for some of the substances discussed in this paper and is extracted from a long table given by Walden, serves to show the kind of agreement that may be expected.

[*] *Zeit. Phys. Chem.* lxv. p. 129 (1909).

TABLE IV.

Substance.	K.	a.	1·21 K.	$\dfrac{0 \cdot 94}{K}$.	$\dfrac{1 \cdot 16}{a}$	Mean.	θ_c obs.
Ether	·00516	·00603	·00624	182°	192°	187°	194°
Methyl formate	·00435	·00553	·00526	216	210	213	214
Ethyl acetate............	·00392	·00463	·00474	240	250	245	250
Carbon tetrachloride ..	·00337	·00418	·00408	279	278	278·5	283
Benzene................	·00329	·00416	·00398	286	279	283	288·5
Chloro-benzene.........	·00266	·00311	·00322	353	373	363	359
Ethyl propionate	·00331	...	·00400	284	...	284	273
Bromine	·00298	·00381	·00361	315	305	310	302

The meaning of the column headed 1·21 K—which is an addition to Walden's table—will be explained later. It is evident that the agreement between the numbers in the last two columns is only approximate, and equation (iii.) is so much more exact in use, that it removes any further necessity for the employment of the very approximate equations (viii.).

The reason for the variability of the "constants" of equations (viii.) is not far to seek. The coefficient a is not really a constant, but is a function of the temperature θ. If we expand equation (iii.) we see that, very approximately, and for low temperatures

$$a = nb = 1 \cdot 21 \, b,$$

where b is accurately the reciprocal of the critical temperature. We thus obtain

$$a\theta_c = 1 \cdot 21, \quad . \quad . \quad . \quad . \quad . \quad \text{(ix.)}$$

in fair agreement with Walden's empirically found relation $a\theta_c = 1 \cdot 16$. Neither of these expressions, however, can be considered as anything but a rough approximation on account of the neglect of squares and higher powers in the expansion of (iii.).

Ramsay and Shields have remarked that for many substances *capillary-rise* is approximately a linear function of the temperature right up to the critical point. In which case we have

$$h = h_0(1 - b\theta), \quad . \quad . \quad . \quad . \quad . \quad \text{(x.)}$$

and therefore, remembering that at ordinary temperatures (and assuming a zero contact-angle) we may write $a^2 = rh$, we have

$$\frac{a^2}{a_0{}^2} = \frac{h}{h} = (1 - b\theta).$$

Hence it is evident that

$$\mathrm{K} = b, \quad \text{or} \quad \mathrm{K}\theta_c = 1,$$

again in fair agreement with Walden's equation $\mathrm{K}\theta_c = 0 \cdot 94$. Hence, very roughly, the relation between the coefficients α and K is

$$\alpha = n\mathrm{K} = 1 \cdot 21\,\mathrm{K}.$$

The values of $1 \cdot 21\,\mathrm{K}$ have been calculated and placed in the fourth column of Table IV., and it will be seen that the agreement is as close as one could expect. The reason, therefore, for the variability of Walden's results seems to lie in the fact that the coefficient α is a function of the temperature, while the assumption of proportionality between α and the reciprocal of the critical temperature demands that α shall be independent of the temperature. In fact α is *not* rigorously equal to nb but is given by

$$\alpha = nb - \frac{n(n-1)}{1 \cdot 2}\,b^2\theta + \ldots ,$$

and the remaining terms of the expansion are quite appreciable even at moderate temperatures.

It may then be considered that for unassociated liquids equation (iii.) holds with very considerable accuracy, and may safely be used to estimate critical temperatures, even if the observations of surface-tension have only been made over a limited range of temperature. But it must be remembered that in all the cases considered the surface-tension measured is that of the liquid in contact with its own vapour, and it remains to be seen whether the formula holds for liquids in contact with *air*. In most cases the surface-tension of a liquid in contact with air differs very slightly from that of a liquid in contact with its own vapour, and this difference would hardly be expected to be sufficient to invalidate the formula. Unfortunately the data at my disposal for capillary-rise in presence of air are somewhat scanty and scattered, and I have therefore restricted myself to a discussion of the numbers furnished by the careful experiments of Mr. J. L. R. Morgan [*] on the drop-weights of various liquids. Assuming proportionality between drop-weights and surface-tension for drops falling from the same tip, we have

$$w = w_0(1 - b\theta)^n \quad \ldots \quad \text{(xi.)}$$

[*] See, in particular, Morgan & Higgins, Journ. Amer. Chem. Soc. xxx. p. 1055 (1908), and Morgan & Schwartz, xxxiii. p. 1041 (1911) in the same journal.

as the equation to be tested. In comparing experiment with theory I have, for simplicity in calculation, assumed in every case that n has its mean value 1·21, while for the value of b I have simply taken the reciprocal of the known critical temperature. Values of w (the weight of a single drop at θ°) were then calculated from (xi.) and compared with the observed values. Better results would probably be found by calculating values of b and of n for each substance separately, but the agreement as shown in Tables V., VI., and VII. is sufficiently good to prove the validity of the formula.

<div style="display:flex">

TABLE V.

Benzene.

$b = ·003466, w_0 = ·03699$ gm.

θ.	w obs.	w calc.	Diff.
11°·4	·03524	·03523	−·00001
30·2	·03235	·03235	±·0000
53·0	·02887	·02894	+·00007
68·5	·02653	·02664	+·00011

TABLE VI.

Methyl formate.

$b = ·004673, w_0 = ·02991$ gm.

θ.	w obs.	w calc.	Diff.
6°·7	·02886	·02878	−·00008
10·0	·02824	·02822	−·00002
16·4	·02736	·02716	−·00020
27·8	·02561*	·02527	−·00034

</div>

TABLE VII.

Chloro-benzene.

$b = ·002784, \quad w_0 = ·04226$ gm.

θ.	w obs.	w calc.	Diff.
8°·2	·04108	·04110	+·00002
39·2	·03663	·03676	+·00013
50·8	·03499	·03514	+·00015
63·9	·03320	·03334	+·00014
72·2	·03205	·03221	+·00016

It remains to discuss the effect of composition and constitution on the values of b and of n. The variation in n is

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* Misprinted in the original paper (Morgan & Schwartz, *l. c.* p. 1047) as ·02661 gm. The formula served to detect the error, as the difference seemed to be too great to be accounted for by errors in either formula or experiment. Recalculating from the fundamental observations given in the paper, the mistake was found to be due to a slip in the arithmetical work.

very small, and as far as can be seen from the figures in Table I. is quite irregular. As errors in setting the ruler have a marked effect on the value of n, it is quite possible that, had the experimental results been treated by some more exact method, the variations in n would show regularities not here apparent. But the labour of such calculations would have been out of all proportion to the slight gain in accuracy, and for our purposes—the accurate representation of the temperature-variation of surface-tension, and the calculation of the critical temperature from surface-tension observations carried out at ordinary temperatures—it is sufficient to note that the variation in n is very slight, and that the mean value of n is about 1·21.

As far as b is concerned, the discussion practically resolves itself into a consideration of the effect of constitution on the critical temperature. Table I. shows clearly that in the case of the esters $R \cdot COO\ R_1$ b diminishes—*i. e.*, the critical temperature increases—with increase of R or R_1 (the other radicle meanwhile being supposed constant). Also the value of b for an iso-compound is greater than the value for the normal ester—*i. e.*, the critical temperature is lower.

Again, R and R_1 are not mutually interchangeable. For example, we have

$$C_2H_5 \cdot COOCH_3 \quad \ldots \quad b = ·003891$$
$$CH_3 \cdot COOC_2H_5 \quad \ldots \quad b = ·003984$$

and

$$C_3H_7 \cdot COOCH_3 \quad , \ldots \quad b = ·003559$$
$$CH_3 \cdot COOC_3H_7 \quad \ldots \quad b = ·003623$$

In each case the transference of the more complex radicle to the carboxyl group increases the value of b; the effect is, however, much less pronounced in the second case than the first, and probably decreases with increasing complexity of R and R_1.

If we denote by γ the ratio of the absolute critical temperature to the absolute boiling-point at normal pressure, I have elsewhere shown that for the normal paraffins [*]

$$\gamma n^g = h,$$

where g and h are constants, and n the number of carbon atoms in the molecule. The experimentally observed values

[*] Phil. Mag. April 1915, p. 602.

for γ for the esters here examined are given in Table VIII., and it will be seen that as R_1 increases (R being constant) γ steadily decreases, and that a similar result holds good for increase of R (R_1 being constant).

<div align="center">TABLE VIII.</div>

Substance.	B. point obs.	θ_c obs.	$\gamma = \dfrac{\theta_c}{\theta}$.
Methyl formate	304·9	487·0	1·597
Methyl acetate	330·2	506·7	1·535
Methyl propionate ...	352·7	530·4	1·504
Methyl butyrate	375·8	554·3	1·475
Ethyl formate	327·3	508·3	1·553
Ethyl acetate	350·1	523·1	1·494
Ethyl propionate	371·8	545·9	1·469
Propyl formate.........	353·9	537·9	1·520
Propyl acetate	370·6	549·2	1·467

The data are somewhat too few in number to establish quantitative laws with much confidence, but it may be noticed that for the series $RCOOCH_3$ the relation between γ and n (the number of carbon atoms in R) is very accurately linear, leading to the result

$$c\gamma = d - n, \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xii.)}$$

where c and d are constants. In this case $d = 52 \cdot 17$ and $c = 33 \cdot 33$; the agreement between the calculated and observed values of γ is shown in Table IX. From this result

<div align="center">TABLE IX.</div>

n.	γ observed.	γ calculated.	b (from xiii.).	b (from iii.).
0	1·597	[1·565]	[·004897]	·004695
1	1·535	1·535	·004276	·004274
2	1·504	1·505	·003879	·003891
3	1·475	1·475	·003555	·003559

it easily follows that the temperature coefficient of surface-tension—b in equation (iii.)—is connected with the absolute boiling-point of the substance considered by the relation

$$b = \frac{c}{(d-n)\theta - 273c} = \frac{33 \cdot 33}{(52 \cdot 17 - n)\theta - 9100} \cdot \cdot \quad \text{(xiii.)}$$

Columns 4 and 5 of Table IX. show the agreement between the values of b calculated from (xiii.) and those given directly from the surface-tension observations. It is very probable that with more extended data the *form* of this relation between θ and b will be altered, but the fact remains that there is a definite relation between the absolute boiling-point of an unassociated liquid and the temperature coefficient of its surface-tension, so that this temperature coefficient may be calculated from observations of the boiling-point alone.

It may be remarked in conclusion that associated liquids so far as I have tested them do not agree with equation (iii.) —in fact, agreement with (iii.) may form a very convenient test of non-association. I hope to return to this point later.

University College of North Wales,
Bangor.
July 1915.

IV. *On Discontinuous Wave-Motion.*
By C. V. Raman, *M.A., and* S. Appaswamaiyar *.

[Plate I.]

A N analytical discussion of the principal mode of vibration of a bowed string as ascertained from the form of its vibration-curves, leads to the result that at two epochs in each period of vibration the string should pass as a whole through its position of statical equilibrium, alternately in opposite directions. At the first epoch, according to the analysis, the velocity at every point on the string is proportional to its distance from one end, there being *a discontinuous fall of the velocity to zero* at the other end. At the second epoch the state of matters is reversed, the motion being such that the velocities are proportional to the distances from the farther end, the discontinuous fall being at the nearer. These results are of importance as defining the essentially discontinuous nature of the motion involved, but it is noticed from the literature of the subject† that they are obtained by an elaborate and indirect analytical process from the observed form of the vibration-curves, and have not so far received direct experimental confirmation. Some time ago it occurred to one of us that an experimental test was

* Communicated by the Authors.

† See Riemann and Weber's 'The Partial Differential Equations of Mathematical Physics,' pp. 216–223.

not impracticable and would be of considerable interest, as affording a direct demonstration of the discontinuous distribution of velocity indicated by the analysis. The present paper deals briefly with the method adopted and the results.

The mode of vibration of the string is evidently determined by its configuration and its velocities at either of the two epochs referred to above. If, therefore, it is possible directly to impose at every point of a finite string in its position of equilibrium the initial distribution of velocities with a discontinuity at one end indicated by the analysis, the resulting free oscillations should have the same characteristic vibration-curves as a bowed string. We have found it possible successfully to realize these conditions in experiment by arranging that a stretched string has initially a uniform angular velocity about one end, and that in the course of this motion one point on it impinges upon and is suddenly brought to rest by a fixed stop or bridge provided for the purpose. The length of the string between the fixed extremity and the bridge is thus isolated, and photographs of the vibration-curves of the resulting motion are secured by the following device. By setting a narrow slit across and immediately behind the string in any desired position, and illuminating the slit with the light from an electric arc, any given point on the string can be caused to record its motion photographically on sensitive paper contained in a dark slide which is caused to move in a direction parallel to the string, *i. e.* vertically downwards, with uniform velocity behind the illuminated slit. The necessary movement of the string itself is secured by drawing it to one side together with the weight attached to its free end, and allowing it to swing down in the manner of a pendulum before one point on it comes up against a fixed stop, which is placed about three-fourths of the way down between the upper fixed extremity and the free end. The shadow of the string across the slit records itself on the photographic paper as a white curve on a dark ground. Six records obtained in this manner are reproduced in Plate I. One of the points of observation chosen was the centre of the string and the others were on either side of it.

It will be noticed that the records show the motion at each of the points of observation, both before and after the first impulse set up by the impact reaches it. The velocity at every point in the initial motion is exactly the same as the velocity of the upward motion in the vibration-curves. The form of the vibration as shown by the records evidently

reproduces that of a bowed string in a very perfect manner, the discontinuous changes of velocity being clearly shown. Though the motion is a free oscillation, it remains practically unaltered in form for a considerable number of periods, and the experiment can thus be readily projected on the screen, and is suitable for lecture demonstration.

We shall now briefly consider the theory of the experiment described above from two distinct points of view. First, *by application of the Fourier Analysis*: Taking the originally fixed end as the origin $(x = 0)$ and the position of the string at time $t = 0$ as the axis of x, we obtain the expansion

$$y = a_1 \sin \frac{\pi x}{l} \sin \frac{2\pi t}{T} + a_2 \sin \frac{2\pi x}{l} \sin \frac{4\pi t}{T} + \&c.,$$

in which the cosine terms are entirely absent, y being equal to zero when $t = 0$. The values of the coefficients a_1, a_2, &c. have to be found from the initial condition $\left(\dfrac{dy}{dt}\right)_{t=0} = \omega x$. By expanding ωx in a series of sines, differentiating the expression for y, and putting $t = 0$, we obtain

$$\left(\frac{dy}{dt}\right)_{t=0} = \frac{2\pi}{T}\left(a_1 \sin \frac{\pi x}{l} + 2a_2 \sin \frac{2\pi x}{l} + \&c.\right)$$

$$= \frac{2l\omega}{\pi}\left(\sin \frac{\pi x}{l} - \tfrac{1}{2} \sin \frac{2\pi x}{l} + \&c.\right).$$

The values of the coefficients may now be written down :

$$a_1 = \frac{l\omega T}{\pi^2}, \quad a_2 = -\frac{1}{4}\frac{l\omega T}{\pi^2},$$

and so on. Finally we have

$$y = \sum_{n=1}^{n=\infty} (-1)^{n-1} \frac{l\omega T}{n^2\pi^2} \sin \frac{n\pi x}{l} \sin \frac{2\pi n t}{T}.$$

To find the character of the motion expressed by the series, we have to effect its summation. This is best done by differentiating the series and writing it in the form

$$\frac{dy}{dt} = \sum_{n=1}^{n=\infty} (-1)^{n-1}\frac{l\omega}{n\pi}\left[\sin n\pi\left(\frac{x}{l} - \frac{2t}{T}\right) + \sin n\pi\left(\frac{x}{l} + \frac{2t}{T}\right)\right].$$

The two series into which the expansion has thus been split up may be summed independently and then added together. It will suffice to trace the value of $\frac{dy}{dt}$ over times ranging from $t=0$ up to $t=T$, as the values subsequently repeat themselves. At any given point x_0 on the string, the velocity $\frac{dy}{dt}$ remains at its initial value ωx_0 from $t=0$ up to the time $t=\frac{T}{2}\frac{l-x_0}{l}$. It then suddenly changes to the value $-\omega(l-x_0)$, at which it remains up to the time $t=\frac{T}{2}\frac{l+x_0}{l}$. The velocity then suddenly regains its original value ωx_0, which it retains up to the end of the complete period T. From these values the configuration of the string may be constructed, and is seen to consist of two straight lines meeting sharply at a point which travels with uniform velocity $\frac{2l}{T}$ along two parabolic arcs situated one on either side of the string. As the edge or angle in the configuration of the string passes over any point on it, the velocity at that point suddenly alters by the quantity $l\omega$. This sudden alteration of velocity is evidently due to the resultant of the forces acting on the element of the string over which the edge passes being infinite in proportion to its mass, and in this we may trace the propagation of the impulse originally sent out by the impact on the bridge.

Secondly, *by the geometrical method* : Since the impulse set up by the sudden stoppage of the motion at the bridge should evidently travel with the ordinary velocity of wave-propagation, the character of the motion can be found from purely geometrical considerations without the aid of the Fourier Analysis, and this is really the more instructive method of considering the problem. The solution of the equation of wave-propagation on an infinite string not subject to damping is

$$y = f(x-at) + F(x+at).$$
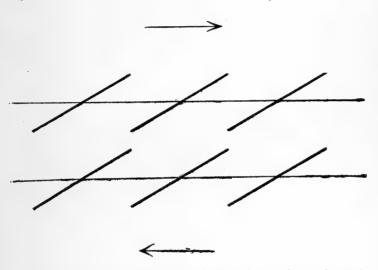
Differentiating with respect to time, we have

$$\frac{dy}{dt} = -af'(x-at) + aF'(x+at).$$

If the two terms on the right-hand side of this equation are periodic functions with wave-length equal to $2l$, and are so

related that at the two points $x=0$ and $x=l$, $\dfrac{dy}{dt}$ has always
zero value, the velocity at any point on the finite string in
the actual case can be found for any instant during the
vibration by summation of the values of the two functions.
At time $t=0$, in the experiment described, the initial dis-
placements of the string from the position of equilibrium
are everywhere zero, and we may therefore take half the
initial velocity at each point for the positive velocity-wave
and the other half for the negative velocity-wave, and the
two waves may be constructed in the manner shown in the
figure below.

By superposing the waves after shifting them through
equal distances in opposite directions, the character of the
motion at every point on the string can be found by inspec-
tion, and the configuration of the string can be found from
the known velocities and the times during which they subsist.
The geometrical construction shown in the figure emphasizes
the fact that the case is essentially one of the propagation of
a discontinuous wave.

The experiments described in this note were first made at
the Presidency College, Madras.

V. *A Note on the Relation between the Thermal Conductivity
and the Viscosity of Gases with reference to Molecular
Complexity.* By J. A. POLLOCK, *D.Sc., Professor of
Physics in the University of Sydney* [*].

IN the equation $k = f \eta c_v$, expressing the thermal conduc-
tivity of a gas in terms of the viscosity and specific
heat, the coefficient f is a numerical factor which is approx-
imately constant for gases of the some atomicity. Such a
fact suggests the probability of a relationship between f and
γ, the ratio of the specific heats. But long before the result,
just mentioned, was fully established, the probability of f
being a function of γ was recognized, though it was
not generally appreciated. As early as 1876 Boltzmann[†],
from theoretical considerations, obtained the expression
$f = 3 f'(\gamma - 1)/2$, where f' is the constant for monatomic
gases. It has been known for some time that the equation is
physically inaccurate, but the matter does not seem to have
been followed further.

Recently new results for the thermal conductivities of a
number of gases have been published by Eucken[‡]. In con-
nexion with these measures, Eucken discusses the dependence
of f, not only on the properties of the molecule, but also on
the temperature. As possibly lying outside the main lines of
his investigation, he does not consider the relationsip of f to
γ, but, from the zero temperature values of the thermal con-
ductivities and viscosities given by him, a relation appears to
exist between the two factors which can be expressed by an
equation of the form

$$f = \frac{a(\gamma - 1)}{\gamma^n},$$

where a and n are constants. The precise arithmetical
adjustment of these constants may well await further
measures ; in the meantime, with numerical simplicity as
well as physical accuracy in view, the equation may be
written

$$f = \frac{7 \cdot 32 (\gamma - 1)}{\gamma^{1 \cdot 3}}.$$

If, in the original expression, n, the power of γ, is put

[†] Boltzmann, Pogg. *Ann.* clvii. p. 457 (1876); see also Schleiermacher,
Wied. *Ann.* xxxvi. p. 346 (1889); and Chapman, Trans. Roy. Soc.
ccxi. A. p. 433 (1912).
[‡] Eucken, *Phys. Zeitschr.* xiv. p. 324 (1913).

equal to unity, the equation, with an appropriate value of the constant, quite well represents the experimental results with the exception of those for the monatomic gases. This leads, in the case of perfect gases, to the simple relation

$$\frac{m\gamma k_0}{\eta_0} = \text{constant},$$

where m is the molecular mass.

In the following table, with the zero temperature measures of k and η, taken from Eucken's paper, I give, for the calculation of f, the experimental results for c_p and γ instead

TABLE I.

1	2	3	4	5	6
Molecule.	m.	$k_0 \times 10^6$.	$\eta_0 \times 10^6$.	c_p.	γ.
He	4	336	187·6	1·260*	1·63
A	40	39·0	210·2	0·123	1·667
H_2	2	397	85	3·422†	1·402†
N_2	28	56·6	167·6	0·2429†	1·412†
O_2	32	57·0	192·2	0·2173†	1·402†
Air	29	56·6	171	0·2376†	1·405†
Cl_2	71	18·29	123·7	0·115	1·323‡
CO	28	54·25	167·2	0·2502*	1·401
NO	30	55·5	179·4	0·232	1·394
H_2S	34	30·45	118·4	0·245	1·340
CO_2	44	33·7	138	0·2010	1·300
N_2O	44	35·15	136·2	0·213	1·324
SO_2	64	19·5	118·3	0·1544‡	1·256
CS_2	76	16·15	92·4	0·160	1·239
NH_3	17	51·35	92·6	0·520	1·336
C_2H_2	26	44·0	94·3	...	1·26
CH_4	16	71·45	102·9	0·591	1·313
C_2H_4	28	40·7	90·66	0·404	1·264
C_2H_6	30	42·6	85·5	...	1·22

* Scheel and Heuse, *Ann. d. Physik*, xl. 3, p. 473 (1913). † Escher, *Ann. d. Physik*, xlii. 4, p. 761 (1913). ‡ Landolt-Börnstein Tabellen. All other values in columns 5 and 6, from Kaye and Laby's Tables.

of the values of c_v. The figures given for f in column 2 of Table II., deduced from the equation $k = f\eta c_p/\gamma$, are thus wholly dependent on the results of experiment.

In this second table, the values of f, derived from the expression $f = 7·32(\gamma-1)/\gamma^{1·3}$, are entered in column 3. An idea of the physical accuracy of the calculated results may, therefore, be obtained from a comparison of these figures

TABLE II.

	1	2	3	4
	Molecule.	f obs. $\dfrac{\gamma k_0}{\eta_0 c_p}$	f cal. $\dfrac{7 \cdot 32\,(\gamma-1)}{\gamma^{1 \cdot 3}}$	$\dfrac{m\gamma k_0}{\eta_0}$
	He	2·32	2·45	11·6
	A	2·51	2·51	12·4
	H_2	1·91	1·90	13·2
	N_2	1·96	1·93	13·4
	O_2	1·91	1·90	13·3
	Air	1·96	1·91	13·5
	Cl_2	1·70	1·63	13·8
	CO	1·82	1·89	12·7
	NO...............	1·90	1·87	12·9
	H_2S	1·41	1·70	11·7
	CO_2	1·58	1·56	14·0
	N_2O	1·60	1·65	15·0
	SO_2	1·35	1·39	13·3
	CS_2	1·35	1·32	16·5
	NH_3	1·79	1·69	12·6
	C_2H_2	...	...	15·3
	CH_4	1·52	1·61	14·6
	C_2H_4	1·40	1·43	15·9
	C_2H_6	...	...	18·3

with those in column 2. There are certainly large differences between the calculated and observed values for some gases, but the experimental determinations cannot be considered in all cases as final.

The last column of Table II. contains the values of $m\gamma k_0/\eta_0$. As previously mentioned, with the present experimental results, constancy of the value of the ratio is only to be expected in the case of perfect gases with molecules of an atomicity greater than 2. The approximate similarity of the figures in some number of instances is, therefore, perhaps more remarkable than the divergencies in the other cases.

It is interesting to note the rise that has taken place in the values of the thermal conductivities. For many years the determinations of f for diatomic gases were cited in support of Meyer's well-known theoretical deduction, $f = 1·6027$. Now, from Eucken's measures of the thermal conductivities, the value of f for these gases is 1·9.

The University of Sydney,
    September 20th, 1915.

VI. *Some Observations on the Absorption Spectra of the Vapours of Inorganic Salts.* By E. J. EVANS, *B.Sc., A.R.C.S., Lecturer in Physics, Victoria University, Manchester* *.

[Plate II.]

INTRODUCTION.

SOME time ago the present author† published investigations on the absorption spectra of the vapours of iodine, bromine, selenium, and tellurium at various temperatures, and later, as a continuation of the above investigations, the absorption spectra of the vapours of certain simple salts were examined. This research was not completed, as the author's attention was diverted to other problems, and the object of the present paper is to give a brief account of the results then obtained.

It is well known that the absorption spectra of the above-mentioned elementary substances show the presence of well-defined absorption bands, and it was considered of some interest to determine whether the absorption spectra of the vapours of a few inorganic salts show the presence of similar bands. For this purpose the absorption spectra of the chlorides of ammonium and mercury, and the chloride, bromide, and iodide of cadmium were examined. It was found that all the vapours examined, with the possible exception of ammonium chloride, showed evidence of a general selective absorption in the ultra-violet, and in no case could it be definitely proved that the vapours of the salts gave any well-defined absorption bands similar to those of Cl, Br, and I.

These conclusions refer to the particular region of the spectrum (λ 2500–λ 6700) which was investigated. No measurements of the variation of the general absorption with wave-length were made.

EXPERIMENTAL ARRANGEMENT.

A weighed quantity of the salt under investigation was placed in a quartz tube, which was evacuated to a low pressure through a side-tube connected to a mercury pump. The side-tube was then sealed off in the oxy-hydrogen flame. The quartz tube was afterwards placed at the centre of an

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* Communicated by Sir E. Rutherford. This paper formed a portion of a thesis approved for the D.Sc. degree by the University of London.

† Astrophys. Journal, xxxii. pp. 1–16 (1910); xxxii. pp. 291–299 (1910); xxxiv. pp. 277–287 (1911); xxxvi. pp. 228–238 (1912).

electric furnace wound with nichrome wire, and the temperature could be adjusted to any value between that of the room and about 1200° C. The temperature was measured by a Pt, Pt—Rh thermocouple, which was connected to a direct reading instrument. When the required temperature had been attained, light from the positive pole of the carbon arc was passed through the vapour inside the quartz tube, and focussed by quartz lenses on the slit of a concave grating, having a radius of 1 metre, and ruled with 15,000 lines to the inch. The spectrum was then examined both visually and photographically.

Experimental Results.

Ammonium Chloride.

It is well known that the vapour of this substance is dissociated into NH_3 and HCl at 350° C., and consequently the pressure of the vapour inside the quartz tube is double the amount calculated from the ordinary gas equation

$$pv = R \frac{M}{m} \theta,$$

where $R = 8\cdot2 \times 10^7$,

θ = absolute temperature,

m = molecular weight of vapour,

M = mass in grams of substance in tube,

v = volume of tube in c.c.

From the dimensions of the tube it could readily be deduced that if ·017 gram of NH_4Cl was placed in the tube, the pressure of the vapour at a temperature of 700° C. was approximately 2 atmospheres, and in the experiments under discussion this quantity of NH_4Cl was used. Photographs of the absorption spectrum were obtained at temperatures varying from 250° C. to 550° C., and visual observations were also made. As the result of a large number of experiments, it was concluded that the vapour of ammonium chloride does not give any well-defined absorption bands in the region extending from λ 2500–λ 6700, and, furthermore, there is no definite evidence that the vapour shows any general absorption in the same region. It is, however, possible that the vapour absorbs in the extreme red and infra-red regions of the spectrum, which were not examined in this research.

Mercuric and Mercurous Chloride.

Mercuric chloride is volatile even at ordinary temperatures, and its vapour pressure increases rapidly with temperature from 20.7 mm. at 200° C. to 370.7 mm. at 2.0° C. In the present experiments .10 gram of mercuric chloride was placed in an evacuated quartz tube, and by means of the gas equation it was calculated that the pressure of the vapour was approximately 1.6 atmospheres at 1000° C. Visual observations and the examination of numerous photographs taken at temperatures ranging from 20° C. to 1000° C. showed that there were no well-defined bands in the region λ 2500–λ 6700. On the other hand, there was distinct evidence of a general absorption in the ultra-violet which increased in intensity and spread towards the red end of the spectrum with rise of temperature. At 900° C. no light of shorter wave-length than λ 3400 passed through the vapour.

Mercurous chloride sublimes at about 400° C., and its vapour consists of a mixture of mercury and mercuric chloride unless special care is taken to free the salt from traces of moisture. About .09 gram of the salt was heated to temperatures varying from 400° C. to 800° C., and the absorption spectrum was photographed and also visually examined.

The photograph taken at 400° C. showed general absorption in the region λ 2500–λ 2800, and this increased with rise of temperature, so that at 800° C. the continuous spectrum of the carbon arc could not be photographed below λ 3200.

As in the case of mercuric chloride, the observations carried out both visually and photographically indicated that the vapour at temperatures varying from 400° C.–800° C. gave no well-defined absorption bands. In the experiments described, no special care was taken to absolutely remove all traces of moisture, and consequently the vapour probably consisted of a mixture of mercury and mercuric chloride. According to the experiments of Wood [*], mercury shows an absorption band at λ 2536 which widens unsymmetrically towards the red over a range of 400 Å.U. as the pressure increases to several atmospheres. If a foreign gas is present, the line widens symmetrically at first, and afterwards unsymmetrically towards the red.

In the experiments on mercurous chloride the presence of the λ 2536 line would be difficult to detect, since the mercury

* Astrophys. Journal, xxvi. pp. 41–45 (1907).

would be mixed with mercuric-chloride vapour, and the continuous spectrum from the carbon arc is very faint below λ 2800.

The Bromide, Iodide, and Chloride of Cadmium.

In the experiments with cadmium bromide, which melts at 571° C. and boils at 809° C., ·07 gram of the salt was placed in an evacuated quartz tube, and it was calculated that the pressure of the vapour was slightly in excess of 1 atmosphere at 1000° C.

Two sets of experiments were carried out at temperatures varying from 600° C. to 900° C., and several photographs of the absorption spectrum were taken. The first series of photographs showed no trace of any cadmium absorption line, but the second series even at 600° showed the presence of the cadmium absorption line at λ 3261. The line was, however, not strong on any of the films, showing that the cadmium bromide had only undergone slight decomposition at the higher temperatures. Apart from this line there were no other absorption lines or bands on the photographs. At 600° C. there was evidence of general absorption below λ 3100, and at 900° C. all wave-lengths between λ 2500 and λ 3800 were completely absorbed by the cadmium-bromide vapour. In later experiments ·065 gram of metallic cadmium were placed in the quartz tube, and a photograph of the absorption spectrum was taken at 1000° C. The quantity of free cadmium present in this experiment was much greater than in the experiments with the cadmium bromide, but even then there was complete absorption only below λ 3000. These experiments, therefore, strongly point to the conclusion that cadmium-bromide vapour shows general selective absorption in the ultra-violet. The absorption due to the cadmium-bromide vapour is shown in Pl. II. photograph 1 (*a*) and (*b*); (*a*) giving the spectrum of the positive pole of the carbon arc, and (*b*) the same spectrum after the light has passed through the vapour at 900° C. The latter photograph shows a general absorption of light of shorter wave-length than 3800 Å.U.

Experiments were also carried out on the absorption of light by the vapour of cadmium iodide, which melts at 404° C. and boils at 714° C. The iodide was produced by the combination of metallic cadmium with iodine contained in a quartz tube, which was heated to a temperature of about

400° C. by means of an electric furnace. The quantity of each substance used was ·005 gram, and it is therefore seen that the cadmium was in excess. The experiments with pure metallic cadmium previously referred to show that at 1000° C. only light of shorter wave-length than λ 3000 was completely absorbed, and in the cadmium-iodide experiments the amount of free cadmium was only $\frac{1}{30}$ that employed in the experiments on the absorption spectrum of cadmium vapour. As the temperature of the furnace was raised, the light after passing through the quartz tube was reddish in colour, and when examined with the spectroscope showed the ordinary absorption spectrum of iodine vapour. This colour, however, completely disappeared when the temperature of the furnace was approximately 400° C., showing that the iodine had combined with the cadmium. A large number of photographs were then taken at temperatures ranging from 400° C. to 1000° C., and it was found that cadmium-iodide vapour showed a decided general absorption in the ultra-violet. At 400° C. there was scarcely any evidence of absorption, as the light from the positive pole of the electric arc could be photographed in the ultra-violet as far as λ 2500. When, however, the temperature of the furnace had reached 650° C. all light of shorter wave-length than λ 3500 had been absorbed, and this absorption spread towards the red end of the spectrum as the temperature was raised to 1000° C., so that absorption could then be traced as far as λ 3800. As cadmium vapour was present in these experiments, it would be expected that the λ 3261 cadmium absorption line would be visible on the photographs, but owing to the great absorption of the iodide, this line could only be seen faintly on one of the films taken, when the temperature of the furnace was 580° C. Even at this comparatively low temperature the wave-length of the line (λ 3261) was near the limit of transmission.

Finally, the absorption of light by cadmium-chloride vapour was studied. This substance melts at 590° C. and boils at 900° C., and the absorption spectrum of its vapour was photographed at temperatures ranging from 600° C. to 1000° C. In these experiments the quartz tube was evacuated to a pressure of ·01 mm. of mercury, and the quantities of the chloride used in two sets of experiments were ·07 and ·045 gram respectively. It was evident from the results of the first series of experiments that the cadmium-chloride vapour had been partially decomposed at high temperatures, for the 3261 line of cadmium appeared with increasing

intensity on photographs taken when the temperatures of
the vapour were 650° C., 840° C., and 980° C.   In addition
to the 3261 absorption line, photographs taken at tempera-
tures above 800° C. showed the presence of more diffuse
absorption lines of shorter wave-length, but later experiments
indicated that the lines could not possibly be attributed to
the chloride.   These lines became more distinct as the
temperature increased, but their investigation was rendered
difficult by the general absorption in the same region pro-
bably due to the chloride vapour.

In the second series of experiments, greater care was
taken to remove moisture from the chloride, and two photo-
graphs taken at 700° C. and 830° C. showed no trace of the
cadmium absorption line.   There was, however, distinct
evidence of general absorption in the ultra-violet, but it was
less intense than the absorption by $CdBr_2$ and CdI_2.   Even
in these experiments a slight decomposition of the vapour
was obtained at a higher temperature (940° C.), and the 3261
absorption line together with the other lines of shorter wave-
length appeared on the photographic film.   At this tempera-
ture all wave-lengths between $\lambda\,3100$ and $\lambda\,2500$ were
almost completely absorbed.

The absorption of cadmium-chloride vapour is illustrated
by photograph (2) (*a*) and (*b*), where (*a*) is the continuous
spectrum due to the positive pole of the carbon arc, and
(*b*) the same spectrum after passing through $CdCl_2$ vapour
at 940° C.   It shows a general absorption of light of shorter
wave-length than 3100 Å.U., and also the presence of
absorption lines at 3261, 3171, 3162, and 3152.   The 3261
line is the well-known absorption line of cadmium vapour,
and the origin of the other lines will be discussed later.

Experiments on the Absorption of Cadmium Vapour.

The two specimens of cadmium used in these experiments
were analysed spectroscopically to test their purity.   The
cadmium was placed in the positive pole of the carbon arc,
and two photographs were taken with the concave grating.
A careful examination of the photographs showed that the
two specimens did not contain any impurities.

Wood * found that the absorption spectrum of cadmium
vapour consisted of two lines at $\lambda\,2288{\cdot}1$ and $\lambda\,3261{\cdot}2$, which
can also be obtained as emission lines.   The former line,

* Wood, Astrophys. Journal, xxix. pp. 211–223 (1909).

which is much the more prominent, was found to broaden perfectly symmetrically when pure Cd was examined, but unsymmetrically when mercury was added. The absorption line at $\lambda 2288 \cdot 1$ attained a width of about 200 Å.U. at the highest temperatures employed, but the $\lambda 3261$ line was never very broad under these conditions. In the present experiments, only the absorption line at $\lambda 3261$ could be obtained, as the carbon arc which was the source of the continuous spectrum is not suitable for the examination of absorption lines in the neighbourhood of $\lambda 2288 \cdot 1$. These experiments on the absorption of the vapour were carried out at different temperatures with each specimen of cadmium, and the amounts of the metal used were $\cdot 015$ gram and $\cdot 065$ gram respectively. The vapour obtained from $\cdot 015$ gram of one specimen gave an absorption line at $\lambda 3261$, which broadened symmetrically with increase of temperature until its width was about 100 Å.U. at 1000° C. At the above temperature the vapour also gave additional absorption lines in the region $\lambda 3000 - \lambda 3200$, and a general absorption in the region $\lambda 2500 - \lambda 3000$, which is possibly due to the broadening of the $\lambda 2288$ line. These absorption lines were the same as those previously obtained when the absorption spectrum of $CdCl_2$ was examined, with the exception that cadmium vapour gave an extra line at 3178.

The vapour obtained from $\cdot 065$ gram of the other specimen gave practically the same absorption spectrum as the above, with the difference that the absorption lines in the region $\lambda 3000 - \lambda 3200$ were very faint and difficult to detect with certainty. It was found, however, that these lines could be more readily obtained if cadmium vapour were mixed with hydrogen. For this purpose hydrogen was allowed to enter an evacuated quartz tube containing $\cdot 03$ gram of cadmium until the pressure was 25 cm. of mercury. Photographs taken when the temperatures of the vapour were 880° and 970° showed the presence of the absorption lines in the region $\lambda 3000 - \lambda 3200$. The wave-lengths of some of these rather diffuse lines were measured, and the approximate values obtained were 3142, 3152, 3162, and 3171 Å.U. It therefore follows that these lines cannot be attributed to the vapour of $CdCl_2$, and the experiments suggest that they may possibly be due to an unstable compound of Cd and H, the lines being produced when the compound dissociates.

Summary.

The absorption spectra of the vapours of ammonium chloride, mercuric and mercurous chloride, cadmium chloride, bromide, and iodide were examined, and it was found :—

- (a) That the vapours did not give any well-defined absorption lines or bands like bromine and iodine in the region $\lambda 2500$–$\lambda 6700$.

- (b) That they gave a general selective absorption in the ultra-violet (except possibly NH_4Cl) which in the case of the cadmium salts was greater for the iodide and bromide than for the chloride.

VII. *On the most Effective Primary Capacity for Tesla Coils. By* W. Morris Jones, *B.Sc., Research Student of the University of Wales*[*].

IT is generally assumed that a Tesla coil gives the best effect (*i. e.* the highest secondary potential for a given primary discharge potential) when the two circuits are so adjusted that, separated, their periods of oscillations are equal. This condition is expressed by the relation $L_1C_1 = L_2C_2$, and is commonly called the condition for "resonance" or "synchronism," though it does not mean that the two periods of the system are equal when the circuits are closely coupled. The above condition appears to have been first arrived at by Drude[†] in a well known memoir on the Tesla coil, and has received general acceptance.

In a recent paper Professor Taylor Jones[‡] has shown that the above condition does not apply if the adjustment is made by varying the primary capacity alone, but that in this case the "optimum" value of C_1 is considerably greater than the resonance value. Taking the secondary potential, when the

resistances are neglected, as given by the expression

$$V_2 = \frac{V_0 L_{21}}{L_1 \sqrt{(1-m)^2 + 4k^2 m}} (\cos 2\pi n_1 t - \cos 2\pi n_2 t)^*, \quad (1)$$

it is shown in the paper referred to that if $k^2 = 0\cdot265$ the optimum primary capacity is $2\cdot128$ times the " resonance " value; and that if $k^2 = 0\cdot36$ (a value specially recommended by Drude along with the " resonance " condition) the optimum capacity is at least twice as great as the resonance value.

It was suggested to me by Professor Taylor Jones that I might test the conclusions by experiment, and also determine experimentally the optimum primary capacity and relative values of the maximum secondary potential for various values of k^2, with a view to obtaining data for a complete test of the theory.

In the experiments about to be described the coupling coefficient was varied by removing turns from the secondary of the Tesla coil. In this process the primary self-inductance L_1 remains constant, and the variation of L_{21} can be easily determined and allowed for. The value of k^2 and the optimum value of m were determined at each stage. The same spark-length was maintained throughout the experiments, so that V_0 could also be regarded as constant.

The Apparatus.

At the beginning of the series of experiments the secondary of the Tesla coil consisted of 192 turns of bare wire (No. 16 S.W.G.) wound on a wooden octagonal frame smeared with paraffin-wax, the immediate supports of the coil being covered with indiarubber tape. Initially the coil was 80 cm. long and the turns were 25 cm. in diameter. The primary coil was of 5 turns of bare wire (No. 12 S.W.G.). The turns, about 30 cm. diameter, were 1 cm. apart and wound on an ebonite frame of the same shape as that supporting the secondary. The primary coil could be removed altogether from, or put into any position over, the secondary, which was always used with its axis vertical. The primary circuit of the Tesla coil contained the primary coil in series with an oil condenser of variable capacity charged by an induction-coil and discharged across a spark-gap. The primary current of the induction-coil was interrupted by a mercury break driven

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* In this expression V_0 is the induction-coil discharge potential, L_{21} is the induction coefficient of the primary on the secondary, k is the coefficient of coupling, m is the ratio $L_2 C_2 / L_1 C_1$, and n_1, n_2 are the frequencies of oscillation of the system.

by a motor, and the discharge terminals of the coil were made of zinc.

To diminish damping due to brush discharge from the terminals of the secondary of the Tesla coil, and to prevent sparking between secondary and primary, the spark-length used was only 1 mm., and this was kept constant throughout the whole series of experiments. Brush discharge was not altogether prevented even by the use of such a short spark-length.

A few preliminary experiments were made to ascertain whether the primary discharge potential was independent of the primary capacity and remained constant provided the spark-length was constant. For this purpose two condensers of widely different capacities were respectively put in series with the spark-gap. Measurements of the discharge potential were taken by means of an electrostatic oscillograph*. From the results obtained for the two capacities used, the discharge potential appeared to be independent of the primary capacity.

Measurement of Frequencies.

All frequencies were measured by a wavemeter. These were usually too high to be registered by the wavemeters in common use in wireless telegraphy, and one suitable for the purposes of the experiments was constructed as follows. A standardized variable condenser was connected in series with a single circular turn (58·16 cm. diameter) of copper wire (·6376 cm. diameter) the self-inductance of which could be calculated from the formula $L = 4\pi R\left(\log_e \dfrac{8R}{r} - 2\right)$. By means of a suitable switch two other coils of two and three turns respectively could be substituted either separately or in series for the single-turn coil. The range of the wavemeter was thus widened, and all the frequencies required to be measured came within this range. The extra coils were standardized by comparison with the single-turn coil. A carborundum detector with telephone connected across the terminals of the condenser was used in all the experiments. The frequencies of the oscillations in these experiments were within the range $·710 \times 10^6$ to $3·28 \times 10^6$.

Measurement of Maximum Potential.

In these experiments comparative measurements were required of the maximum secondary potential that could be developed for various degrees of coupling of the Tesla coil

* E. T. Jones, Phil. Mag. xiv. p. 238 (1907).

circuits, the adjustment being made by varying the primary capacity.

A number of methods were tried for ascertaining when the potential in the secondary was a maximum. One of these consisted in sparking from a secondary terminal to an insulated electrode. The distances at which the sparks just failed to pass to the electrode were taken as indicating the maximum terminal potential for each adjustment of the capacity in the primary circuit. This method, though giving comparative values of the terminal potential, did not appear sensitive enough for the determination of an optimum capacity[*].

The method finally adopted consisted in measuring the distance from the terminal at which a neon tube just failed to glow when held horizontally opposite the upper terminal of the coil, the end of the tube remote from the terminal being well earthed. This method, although the most sensitive of those tried, was not capable of great exactness; and as the potential of the secondary varied slowly in the region of the maximum, the adjustment of the primary capacity to its most effective value was a difficult matter, and could not be made very accurately. The method, however, is one in which practically no disturbance of the conditions is introduced, owing to the fact that the tube glows when at a considerable distance from the terminal of the coil.

To ensure that the distance of the tube from the coil depended upon the terminal potential alone and not upon the length of the coil, a wire about 2 metres long was attached to the upper secondary terminal. This wire projected horizontally from the coil and was suspended by silk cords from the ceiling. The neon tube was held opposite this wire at right angles to its length. Distances were always measured when the tube was in this position. The glow of the tube was affected by the presence of earthed bodies. It was important that the disposition of these bodies near the wire should remain constant during the experiments. This condition was secured by the projecting wire being at a fixed height from the floor, all other conducting bodies (including that of the experimenter) being kept in a fixed position when readings were being taken.

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[*] It may be mentioned that an aluminium-leaf electroscope connected to one of the secondary terminals also shows a distinct maximum as the primary capacity is varied, such that if the capacity is increased or diminished from this value, the deflexion of the leaf falls. There is thus an optimum capacity for " mean square," as well as for " maximum " secondary potential.

The method of taking a reading was as follows:—The tube was first placed at a moderate distance from the secondary terminal, and it was found that it glowed continuously over a considerable range of values of the primary capacity. The distance of the tube was then increased, the range of C_1 diminishing, until the tube failed to glow continuously but flashed out only at the good primary discharges. By this time the range of C_1 was reduced to fairly narrow limits, and the middle point of the range was taken as the optimum primary capacity. The tube was further removed until these isolated flashes just ceased to appear. The distance of the tube from the terminal was then measured, and this distance was taken as a measure of the maximum secondary potential for the given degree of coupling and the given length of spark-gap.

The frequency-ratio of the electrical oscillations of the system, when so adjusted, was found by means of the wave-meter.

Period of the Primary Circuit.

After the capacity had been adjusted to its most effective value, the period of the primary circuit was determined. This was done by means of a " dummy " primary. This coil was similar in all respects to the primary of the Tesla coil. It had the same number of turns and was made of the same wire. The turns were also of the same diameter as those on the primary, and both coils gave the same reading on the wavemeter when connected up respectively to a constant capacity and spark-gap.

The reading obtained with the wavemeter when the " dummy " had been substituted for the primary of the Tesla coil, gave L_1C_1.

Determination of k^2 and L_2C_2.

The coupling coefficient of the primary and secondary circuits was next found. The " dummy " primary coil having been substituted for the primary of the Tesla coil, and the latter removed to a distance of two or three feet, the primary capacity was varied until the circuit came into tune with the secondary, resonance being indicated by the glow of a neon tube attached for the purpose to the lower secondary terminal. By removing the Tesla coil to a sufficient distance, the range of the capacity in the " dummy " circuit over which the tube glowed could be cut down to very narrow limits, and the " dummy " circuit adjusted fairly accurately to resonance with the secondary. This tuning

adjustment was made when the primary circuit of the Tesla coil was open and also when it was closed by a short wire of sufficient length to allow for the self-inductance of the leads used when the primary was connected up in series with the condenser and spark-gap. The resonance capacity in the dummy circuit was noted in each case. The ratio of the periods when these capacities were respectively in the circuit were obtained from the wavemeter readings. If T_0^2 and T_1^2, to which the wavemeter readings are directly proportional, represent the periods of the secondary when the primary was respectively open and closed, then $T_1^2/T_0^2 = 1 - k^2$ from which k^2 can be immediately obtained. The value of k^2 was also verified in some instances by determining the minimum ratio of the oscillation-frequencies of the Tesla coil system.

The reading of the wavemeter when the " dummy " circuit had been tuned to resonance with the secondary of the Tesla coil, the primary being open, gave the period of the secondary, and therefore the value of $L_2 C_2$. The capacity in the " dummy " circuit for this case was the " resonance " capacity satisfying the condition $L_1 C_1 = L_2 C_2$. The " optimum " primary capacity was found to be always greater than the resonance value.

The above completed the set of determinations required for one value of k^2. The coupling was next increased a little by removing turns from both ends of the secondary, and the primary capacity again adjusted to the " optimum." The whole set of observations was then repeated. These adjustments and observations were made both with the primary coil at the middle of the secondary and the secondary terminals insulated, and with the primary at the lower end of the secondary and the lower terminal of the latter well earthed.

In the earlier part of the series of experiments all the five turns of the primary coil were used ; but when about 100 turns had been removed from the secondary, it was found that the " resonance " value of C_1 became inconveniently small for the range of the oil condenser. Consequently, in the latter part of the series only four turns of the primary coil were used. This reduces L_1 and proportionately increases the " resonance " value of C_1, thus making it more suitable for the range of the oil condenser employed.

The removal of a turn from the primary has, however, another effect. It diminishes L_{21} and L_1, but L_1 is reduced in a greater proportion than L_{21}. Thus the ratio L_{21}/L_1 is increased; and according to the expression (1) the maximum

secondary potential (for given values of m and k^2) should be increased by the removal of one of the primary turns. This was found to be the case, the greatest distance at which the tube glowed being considerably greater with the 4-turn than with the 5-turn primary for the same value of k^2.

It was thought desirable to reduce the results of the later experiments (those made with the 4-turn primary) so as to show what the tube-distance d would have been if the primary coil had remained at 5 turns. In making this correction it was assumed that the maximum secondary potential was proportional to L_{21}/L_1. The correction was therefore made by multiplying the later values of d by the ratio of the old to the new value of L_{21}/L_1.

This was determined as follows:—The change in L_1 was found with the help of the wavemeter, the ratio of the periods of a condenser being found when its terminals were connected to 4 turns and 5 turns respectively of the "dummy" coil. The change in L_{21} was found by ballistic galvanometer experiments, the secondary being connected to the galvanometer and the deflexion observed on the reversal of a given current in the primary, this being done both for 4 turns and for 5 turns.

In this way it was found that the ratio of the old to the new value of L_{21}/L_1 was $\frac{9}{10}$: consequently, in the results given below the values of d obtained with the 4-turn primary have all been reduced by 10 per cent.

At the beginning of the series of experiments the number of turns on the secondary was 192, and this number was reduced by small stages until there remained only 54. During this process the induction coefficient L_{21} gradually diminished, very slowly at first, more rapidly as the number of turns became smaller. Since it was part of the object of the present experiments to determine how the maximum secondary potential varies with k^2, it was necessary to make allowance for the variation of L_{21}, which is one of the factors to which V_2 is proportional. The value of the coefficient L_{21} was therefore determined (in arbitrary units) at each stage by ballistic galvanometer experiments, in which the primary was connected to the galvanometer, and the reversed current sent through the secondary. This was done with the primary at the middle, and also at the lower end of the secondary. Curves were drawn showing how the deflexions varied with the number of turns on the secondary. They showed that the mutual induction between primary and secondary was not sensibly altered until the number of turns had been reduced to 100 when the primary

was at the middle, and 65 with the primary at the lower end of the secondary. By means of these curves corrections could be applied to the values of d due to change in L_{21} caused by the removal of turns from the secondary coil.

TABLE I.

Primary coil over middle of secondary.
Secondary terminals insulated.
Primary spark-length $= 1$ mm.

k^2.	$m(=L_2C_2/L_1C_1)$.	n_2/n_1.	Max. distance d in cm.
0·147	0·740	1·53	65·0 ?
0·166	0·725	1·52	69·0
0·182	0·694	1·53	67·0
0·206	0·588	1·65	63·7
0·222	0·608	1·67	58·0
0·259	0·553	1·80	48·5
0·276	0·551	1·83	48·0
0·307	0·420	2·08	40·0
0·336	0·447	2·08	29·0
0·314	0·437	2·10	40·3
0·368	0·310	2·43	28·8
0·374	0·294	2·50	23·0

TABLE II.

Primary at lower end of secondary.
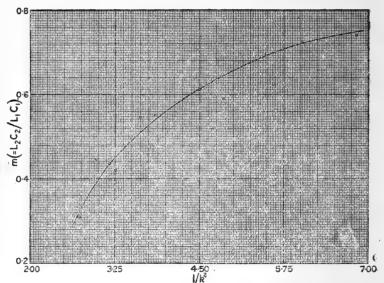Lower terminal of secondary earthed.
Primary spark-length $= 1$ mm.

k^2.	$m(=L_2C_2/L_1C_1)$.	n_2/n_1.	Max. distance d in cm.
0·115	0·830	1·48	146
0·138	0·793	1·50	137
0·154	0·619	1·61	125
0·170	0·580	1·71	115
0·181	0·560	1·73	110
0·200	0·585	1·73	99
0·226	0·470	1·89	94
0·247	0·553	1·87	88
0·237	0·480	1·92	85
0·266	0·373	2·18	77
0·325	0·250	2·56	63

The results obtained are given in Tables I. and II. The first column gives the values of k^2, the second the values of m required to produce the maximum secondary potential, and the third column the values of the frequency-ratio n_2/n_1 when the primary capacity was at the optimum value. The

fourth column gives the maximum distances at which the neon tube glowed. The last three values of d in each table have been reduced, as explained above, by 10 per cent. The distances are measures of the maximum potential that can be developed in the secondary for the corresponding values of k^2 and m, and a primary spark-length of 1 mm.

The results in column 2 of the tables are plotted as curves in figs. 1 and 2, in which the abscissæ represent $1/k^2$ and the ordinates the values of m. Some of the points do not lie well on the curves. This is due to the difficulty of accurately adjusting the primary capacity to its optimum value.

Fig. 1.

However, the curves show that, for all the degrees of coupling obtained, L_2C_2/L_1C_1 was less than unity. It is clear from these results that, if the adjustment of the Tesla coil is made by varying the primary capacity alone, then the optimum value of C_1 is greater than the resonance value, the difference between them diminishing with k^2 in accordance with the theory. The tables also show that the frequency-ratio n_2/n_1, when the primary capacity is adjusted to the optimum value, passes through 2 in the neighbourhood of the value $k^2 = 0.265$. This is also in accordance with the theory.
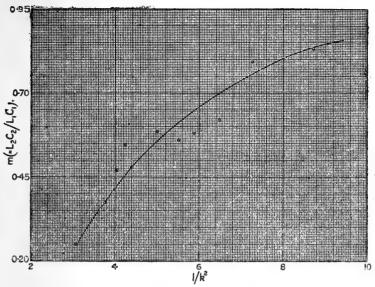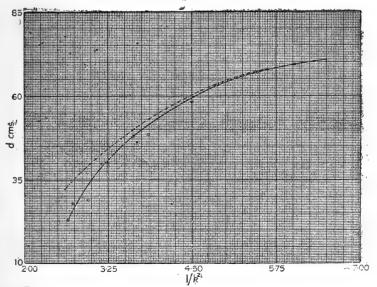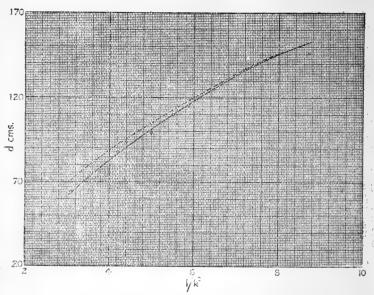
Fig. 2.

Fig. 3.

In figs. 3 and 4 the full-line curves show the tube-
distances d (Tables I. and II., fourth column) plotted
against $1/k^2$. When the correction due to the variation

of L_{21}, caused by removing turns from the secondary coil, is applied, the curves take the form shown by the broken line. The curves show that if V_0, L_{21}, and L_1 are constant, the maximum secondary potential increases as k^2 diminishes.

Fig. 4.
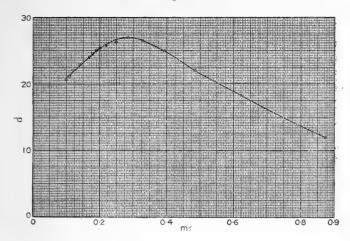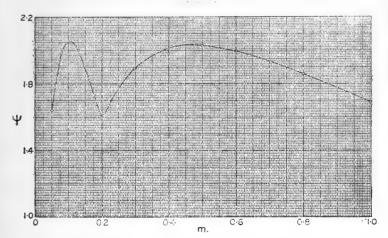
This result also might be anticipated from the theory. By (1) the amplitude of the potential waves in the secondary coil is in this case proportional to $\dfrac{1}{\sqrt{\{(1-m)^2+4k^2m\}}}$. For any value of k this expression has, when $m=1-2k^2$, a maximum value of $\dfrac{1}{2k\sqrt{(1-k^2)}}$. Within the range of the present experiments this quantity increases as k diminishes.

In fig. 5 the curve shows the variation of the maximum tube-distance d with the primary capacity C_1. In this experiment the coils and their coupling coefficient were kept constant, k^2 being $0\cdot348$—nearly equal to the value recommended by Drude. The curve shows a maximum tube-distance near the value $m=0\cdot3$, *i. e.* at a primary capacity much greater than the resonance value given by $m=1$.

Fig. 5.

Fig. 6.

The theoretical curve, obtained by calculation from the expression (1), is shown in fig. 6, also for the case $k^2 = 0.348$. In this curve the ordinate represents the maximum value of the quantity

$$\psi = \frac{1}{\sqrt{\{(1-m)^2 + 4k^2 m\}}} \left(\cos 2\pi n_1 t - \cos 2\pi n_2 t \right)$$

for each value of m, and is therefore proportional to the

maximum secondary potential, since V_0, L_{21}, and L_1 are constant during the experiment. The frequency-ratio n_2/n_1 is calculated from the relation

$$\frac{n_2{}^2}{n_1{}^2} = \frac{m+1+\sqrt{\{(m-1)^2+4k^2m\}}}{m+1-\sqrt{\{(m-1)^2+4k^2m\}}}.$$

There are important differences between the experimental and theoretical curves, figs. 5 and 6. The theoretical greatest maximum occurs at about $m=0\cdot1$, and corresponds approximately to the frequency-ratio $n_2/n_1=4$. This does not appear at all in the experimental curve, in which also the maximum shown occurs at a smaller value of m than does the secondary maximum in the theoretical curve.

It should be remembered, however, that in the expression (1) for the secondary potential, damping due to all causes is neglected, and that the theoretical curve of fig. 6 represents only those maxima which occur near the time $1/2n_1$.

It is possible that in the experiment the damping might be so great in some cases as to diminish these maxima, so that they would not appear as such in the experimental curve. Possibly also the continuation of the experimental curve (fig. 5) to smaller values of m would have revealed some trace of another maximum.

Time did not allow me to determine and allow for the damping factors of the oscillations. With these taken into account better agreement would probably have been found between the curves of figs. 5 and 6.

Similar curves were obtained for the case $k^2=0\cdot255$ and the primary at the lower end of the secondary, and the experimental and calculated curves showed differences similar to those of figs. 5 and 6.

VIII. *Methods for the Summation of certain Types of Series.*
By I. J. Schwatt [*].

I. **T**O find

$$S = \frac{1}{a} + \frac{1}{a(a+1)}r + \frac{1}{a(a+1)(a+2)}r^2 + \ldots = \sum_{n=0}^{\infty} \frac{r^n}{\prod_{\kappa=0}^{n}(a+\kappa)},$$

wherein a is a positive integer.

(i.) We may write

$$S = (a-1)!\sum_{n=0}^{\infty}\frac{r^n}{(a+n)!}$$

$$= \frac{(a-1)!}{r^a}\sum_{n=0}^{\infty}\frac{r^{a+n}}{(a+n)!}$$

$$= \frac{(a-1)!}{r^a}\sum_{n=0}^{\infty}\frac{r^n}{n!}$$

$$= \frac{(a-1)!}{r^a}\left[\sum_{n=0}^{\infty}\frac{r^n}{n!} - \sum_{n=0}^{a-1}\frac{r^n}{n!}\right]$$

$$= \frac{(a-1)!}{r^a}\left[e^r - \sum_{n=0}^{a-1}\frac{r^n}{n!}\right].$$

(ii.) A second method is as follows :

Let u_{n-1} denote the nth term of the given series, then

$$\frac{u_n}{u_{n-1}} = \frac{r}{a+n},$$

and

$$\sum_{n=1}^{\infty}(a+n)u_n = r\sum_{n=1}^{\infty}u_{n-1},$$

or

$$\sum_{n=0}^{\infty}(a+n)u_n = r\sum_{n=0}^{\infty}u_{n+1}.$$

Hence

$$r\frac{dS}{dr} + (a-r)S = 1,$$

and

$$S = e^{-\int\frac{a-r}{r}dr}\left[C + \int\frac{1}{r}e^{\int\frac{a-r}{r}dr}dr\right].$$

$$= \frac{e^r}{r^a}\left[\int e^{-r}r^{a-1}dr + C\right].$$

* Communicated by the Author.

Now

$$\int e^{-r} r^{a-1} dr = -[e^{-r} r^{a-1} + e^{-r}(a-1)r^{a-2}$$
$$+ e^{-r}(a-1)(a-2)r^{a-3} + \ldots + e^{-r}(a-1)!]$$
$$= e^{-r}(a-1)! \sum_{n=0}^{a-1} \frac{r^n}{n!}.$$

Therefore

$$S = -\frac{(a-1)!}{r^a} \sum_{n=0}^{a-1} \frac{r^n}{n!} + C \frac{e^r}{r^a}.$$

Multiplying by r^a and letting $r=0$, we find $C = (a-1)!$
We finally obtain

$$S = \frac{(a-1)!}{r^a}\left[e^r - \sum_{n=0}^{a-1} \frac{r^n}{n!}\right].$$

II. To find

$$S = \frac{1}{1 \cdot 2 \cdot 3} + \frac{1}{3 \cdot 4 \cdot 5} r + \frac{1}{5 \cdot 6 \cdot 7} r^2 + \ldots = \sum_{n=0}^{\infty} \frac{r^n}{(2n+1)(2n+2)(2n+3)}.$$

(i.) Separating the general term into partial fractions

$$\frac{1}{(2n+1)(2n+2)(2n+3)} = \frac{1}{2}\left[\frac{1}{2n+1} - \frac{1}{n+1} + \frac{1}{2n+3}\right],$$

therefore

$$S = \frac{1}{2}\left[\sum_{n=0}^{\infty} \frac{r^n}{2n+1} - \sum_{n=0}^{\infty} \frac{r^n}{n+1} + \sum_{n=0}^{\infty} \frac{r^n}{2n+3}\right],$$
$$= \frac{1}{2}\left[1 + r\sum_{n=0}^{\infty} \frac{r^n}{2n+3} + \sum_{n=0}^{\infty} \frac{r^n}{n+3} - \sum_{n=0}^{\infty} \frac{r^n}{n+1}\right],$$
$$= \frac{1}{2}\left[1 + (1+r)\sum_{n=0}^{\infty} \frac{r^n}{2n+3} + \frac{1}{r}\log(1-r)\right], \quad . \quad (A)$$
$$= \frac{1}{2}\left[1 + \frac{1+r}{r^{\frac{3}{2}}} \sum_{n=0}^{\infty} \frac{r^{\frac{1}{2}(2n+3)}}{2n+3} + \frac{1}{r}\log(1-r)\right].$$

But

$$\sum_{n=0}^{\infty} \frac{r^{\frac{1}{2}(2n+3)}}{2n+3} = \frac{1}{2}\left[r^{\frac{1}{2}} + \frac{r^{\frac{2}{2}}}{2} + \frac{r^{\frac{3}{2}}}{3} + \frac{r^{\frac{4}{2}}}{4} + \frac{r^{\frac{5}{2}}}{5} + \ldots\right.$$
$$\left. + r^{\frac{1}{2}} - \frac{r^{\frac{2}{2}}}{2} + \frac{r^{\frac{3}{2}}}{3} - \frac{r^{\frac{4}{2}}}{4} + \frac{r^{\frac{5}{2}}}{5} - \ldots\right] - r^{\frac{1}{2}}$$
$$= \frac{1}{2}\left[\log(1+r^{\frac{1}{2}}) - \log(1-r^{\frac{1}{2}})\right] - r^{\frac{1}{2}}.$$

Therefore

$$S = \frac{1}{2}\left[1 + \frac{1+r}{2r^{\frac{3}{2}}}\log\frac{1+r^{\frac{1}{2}}}{1-r^{\frac{1}{2}}} - \frac{1+r}{r} + \frac{1}{r}\log(1-r)\right]$$
$$= \frac{1}{4r}\left[\frac{1+r}{r^{\frac{1}{2}}}\log\frac{1+r^{\frac{1}{2}}}{1-r^{\frac{1}{2}}} + 2\log(1-r) - 2\right].$$

(ii.) Another method is the following:

If in form (A) of the preceding method we let

$$r = x^2 \text{ and } \sum_{n=0}^{\infty} \frac{x^{2n+3}}{2n+3} = S_1,$$

then

$$\frac{dS_1}{dx} = \sum_{n=0}^{\infty} x^{2n+2} = \frac{x^2}{1-x^2}.$$

Therefore

$$S_1 = \int_0^x \frac{x^2\,dx}{1-x^2} = \frac{1}{2}\log\frac{1+x}{1-x} - x,$$

and

$$S = \frac{1}{2}\left[1 + \frac{1}{r}\log(1-r) + \frac{1+r}{2r^{\frac{3}{2}}}\log\frac{1+r}{1-r} - \frac{1+r}{r}\right]$$

$$= \frac{1}{4r}\left[\frac{1+r}{r^{\frac{1}{2}}}\log\frac{1+r^{\frac{1}{2}}}{1-r^{\frac{1}{2}}} + 2\log(1-r) - 2\right].$$

(iii.) Still another method is the following:

Let u_{n-1} designate the nth term of the given series, then

$$\frac{u_n}{u_{n-1}} = \frac{n(2n-1)}{(n+1)(2n+3)}\,r,$$

and

$$\sum_{n=1}^{\infty}(n+1)(2n+3)u_n = r\sum_{n=1}^{\infty} n(2n-1)u_{n-1}r,$$

$$= r\sum_{n=0}^{\infty}(n+1)(2n+1)u_n r,$$

and since

$$(n+1)(2n+3)u_n\Big]_{n=0} = \frac{1}{2},$$

therefore

$$\sum_{n=0}^{\infty}(n+1)(2n+3)u_n = r\sum_{n=0}^{\infty}(n+1)(2n+1)u_n + \frac{1}{2},$$

and

$$\left(r\frac{d}{dr}+1\right)\left[2(1-r)r\frac{d}{dr}+3-r\right]S = \frac{1}{2}.$$

Let now

$$\left(r\frac{d}{dr}+1\right)S = y,$$

then

$$2(1-r)r\frac{dy}{dr}+(3-r)y = \frac{1}{2},$$

and

$$y = \frac{1}{4}e^{-\int\frac{3-r}{2r(1-r)}dr}\int_0^r \frac{1}{r(1-r)}e^{\int\frac{3-r}{2r(1-r)}dr}\,dr,$$

$$= \frac{1}{4}\frac{1-r}{r^{\frac{3}{2}}}\int_0^r \frac{r^{\frac{1}{2}}\,dr}{(1-r)^2}.$$

Letting $r = x^2$, and integrating by parts, we have

$$y = \frac{1}{4} \frac{1-r}{r^{\frac{3}{2}}} \left[\frac{1}{r} - \frac{1-r}{2r^{\frac{3}{2}}} \log \frac{1+r^{\frac{1}{2}}}{1-r^{\frac{1}{2}}} \right].$$

Therefore

$$S = \frac{1}{4r} \int_0^r \left[\frac{1}{r} - \frac{1-r}{2r^{\frac{3}{2}}} \log \frac{1+r^{\frac{1}{2}}}{1-r^{\frac{1}{2}}} \right] dr$$

$$= \frac{1}{4r} \left[\frac{1+r}{r^{\frac{1}{2}}} \log \frac{1+r^{\frac{1}{2}}}{1-r^{\frac{1}{2}}} + 2 \log (1-r) - 2 \right].$$

(iv.) A fourth method :

If in the given summation we let $r = x^2$, then

$$S = \sum_{n=0}^{\infty} \frac{x^{2n}}{(2n+1)(2n+2)(2n+3)}.$$

We then have

$$\left(x \frac{d}{dx} + 1 \right) \left(x \frac{d}{dx} + 2 \right) \left(x \frac{d}{dx} + 3 \right) S = \sum_{n=0}^{\infty} x^{2n} = \frac{1}{1-x^2}.$$

Therefore

$$\left(x \frac{d}{dx} + 2 \right) \left(x \frac{d}{dx} + 3 \right) S = \frac{1}{x} \int_0^x \frac{dx}{1-x^2} = \frac{1}{2x} \log \frac{1+x}{1-x},$$

and

$$\left(x \frac{d}{dx} + 3 \right) S = \frac{1}{2x^2} \int_0^x \log \frac{1+x}{1-x} dx$$

$$= \frac{1}{2x^2} \left[x \log \frac{1+x}{1-x} + \log (1-x^2) \right].$$

Hence

$$S = \frac{1}{2x^3} \int_0^x \left[x \log \frac{1+x}{1-x} + \log (1-x^2) \right] dx.$$

Integrating by parts,

$$S = \frac{1}{2x^3} \left[\frac{x^2}{2} \log \frac{1+x}{1-x} + \int_0^x \frac{x^2 dx}{1-x^2} + x \log (1-x^2) \right],$$

$$= \frac{1}{2x^3} \left[\frac{1+x^2}{2} \log \frac{1+x}{1-x} + x \log (1-x^2) - x \right],$$

$$= \frac{1}{4r} \left[\frac{1+r}{r^{\frac{1}{2}}} \log \frac{1+r^{\frac{1}{2}}}{1-r^{\frac{1}{2}}} + 2 \log (1-r) - 2 \right].$$

(v.) We might also arrive at the result in the following way :

Let
$$r = x^2,$$

then
$$x^3 S = S_1 = \sum_{n=0}^{\infty} \frac{x^{2n+3}}{(2n+1)(2n+2)(2n+3)}.$$

Now

$$\frac{d^3S_1}{dx^3} = \sum_{n=0}^{\infty} x^{2n} = \frac{1}{1-x^2},$$

$$\frac{d^2S_1}{dx^2} = \frac{1}{2}\left[\log(1+x) - \log(1-x)\right],$$

$$\frac{dS_1}{dx} = \frac{1}{2}\left[(1+x)\log(1+x) + (1-x)\log(1-x)\right],$$

and

$$S_1 = \frac{1}{2}\left[\frac{1}{2}(1+x^2)\log(1+x) - \frac{1}{4}(1+x)^2\right.$$
$$\left. - \frac{1}{2}(1-x)^2\log(1-x) + \frac{(1-x)^2}{4}\right]$$

$$= \frac{1+x^2}{4}\log\frac{1+x}{1-x} + \frac{x}{2}\log(1-x^2) - \frac{x}{2}.$$

Therefore

$$S = \frac{1+r}{4r^{\frac{3}{2}}}\log\frac{1+r^{\frac{1}{2}}}{1-r^{\frac{1}{2}}} + \frac{1}{2r}\log(1-r) - \frac{1}{2r}$$

or

$$S = \frac{1}{4r}\left[\frac{1+r}{r^{\frac{1}{2}}}\log\frac{1+r^{\frac{1}{2}}}{1-r^{\frac{1}{2}}} + 2\log(1-r) - 2\right].$$

If r is negative, that is, if we are to find

$$S = \frac{1}{1.2.3} - \frac{1}{3.4.5}r + \frac{1}{5.6.7}r^2 - \ldots = \sum_{n=0}^{\infty}\frac{(-r)^n}{(2n+1)(2n+2)(2n+3)},$$

we must substitute in the results obtained above

$$ir^{\frac{1}{2}} \text{ for } r^{\frac{1}{2}}, \text{ and } \log\frac{1+ir^{\frac{1}{2}}}{1-ir^{\frac{1}{2}}} = 2i\tan^{-1}r^{\frac{1}{2}} \text{ for } \log\frac{1+r^{\frac{1}{2}}}{1-r^{\frac{1}{2}}}.$$

We then obtain

$$S = -\frac{1}{4r}\left[\frac{2(1-r)}{r^{\frac{1}{2}}}\tan^{-1}r^{\frac{1}{2}} + 2\log(1+r) - 2\right],$$

$$= \frac{1}{2r}\left[1 - \log(1+r) - \frac{1-r}{r^{\frac{1}{2}}}\tan^{-1}r^{\frac{1}{2}}\right].$$

III. To find

$$S = 1 + \frac{4}{11}r + \frac{4.5}{11.12}r^2 + \frac{4.5.6}{11.12.13}r^3 + \ldots = \sum_{n=0}^{\infty}\frac{\prod\limits_{\kappa=0}^{n-1}(4+\kappa)}{\prod\limits_{\kappa=0}^{n-1}(11+\kappa)}r^n.$$

(i.) First method :

$$\frac{\prod\limits_{\kappa=0}^{n-1}(4+\kappa)}{\prod\limits_{\kappa=0}^{n-1}(11+\kappa)} = \frac{10!}{3!}\frac{(n+3)!}{(n+10)!} = \frac{10!}{3!}\frac{1}{\prod\limits_{\kappa=4}^{10}(n+\kappa)},$$

therefore

$$S = \frac{10\,!}{3\,!} \sum_{n=0}^{\infty} \frac{r^n}{\prod_{\kappa=4}^{10}(n+\kappa)}.$$

But

$$\frac{1}{\prod_{\kappa=4}^{10}(n+\kappa)} = \sum_{\kappa=4}^{10}\frac{A_\kappa}{n+\kappa},$$

and

$$A_\kappa = (-1)^\kappa \frac{1}{(\kappa-4)\,!\,(10-\kappa)\,!} = \frac{(-1)^\kappa}{6\,!}\binom{6}{\kappa-4}.$$

Hence

$$S = 10\binom{9}{3} \sum_{\kappa=4}^{10}(-1)^\kappa\binom{6}{\kappa-4}\sum_{n=0}^{\infty}\frac{r^n}{n+\kappa},$$

$$= 10\binom{9}{3}\sum_{\kappa=4}^{10}(-1)^\kappa\binom{6}{\kappa-4}\frac{1}{r^\kappa}\sum_{n=0}^{\infty}\frac{r^{n+\kappa}}{n+\kappa}.$$

Let $\displaystyle\sum_{n=0}^{\infty}\frac{r^{n+\kappa}}{n+\kappa} = S_\kappa,$

then

$$S_\kappa = \sum_{m=\kappa}^{\infty}\frac{r^m}{m} = \sum_{m=1}^{\infty}\frac{r^m}{m} - \sum_{m=1}^{\kappa-1}\frac{r^m}{m},$$

$$= -\log(1-r) - \sum_{m=1}^{\kappa-1}\frac{r^m}{m}.$$

Therefore

$$S = 10\binom{9}{3}\log(1-r)\sum_{\kappa=4}^{10}(-1)^{\kappa-1}\binom{6}{\kappa-4}\frac{1}{r^\kappa}$$
$$+ 10\binom{9}{3}\sum_{\kappa=4}^{10}(-1)^{\kappa-1}\binom{6}{\kappa-4}\frac{1}{r^\kappa}\sum_{m=1}^{\kappa-1}\frac{r^m}{m}.$$

$$= -840\frac{(1-r)^6}{r^{10}}\log(1-r) + 10\binom{9}{3}\sum_{\kappa=0}^{6}(-1)^{\kappa+1}\binom{6}{\kappa}\sum_{m=1}^{\kappa+3}\frac{r^{m-\kappa+4}}{m},$$

$$= \frac{10\binom{9}{3}}{r^{10}}\sum_{\kappa=0}^{6}(-1)^{\kappa+1}\binom{6}{\kappa}\sum_{m=1}^{\kappa+3}\frac{r^{6-\kappa+m}}{m} - 840\frac{(1-r)^6}{r^{10}}\log(1-r),$$

$$= \frac{840}{r^{10}}\left[-(1-r)^6\log(1-r) - r + \frac{11}{2}r^2 - \frac{37}{3}r^3 + \frac{57}{4}r^4 - \frac{87}{10}r^5 \right.$$
$$\left. + \frac{49}{20}r^6 - \frac{1}{7}r^7 - \frac{1}{56}r^8 - \frac{1}{252}r^9\right].$$

(ii.) Let u_{n-1} designate the nth term of the given series,

then
$$\frac{u_n}{u_{n-1}} = \frac{\prod\limits_{\kappa=0}^{n-1}(4+\kappa)}{\prod\limits_{\kappa=0}^{n-2}(4+\kappa)} \cdot \frac{\prod\limits_{\kappa=0}^{n-2}(11+\kappa)}{\prod\limits_{\kappa=0}^{n-1}(11+\kappa)} r, = \frac{n+3}{n+10}r,$$

and
$$\sum_{n=1}^{\infty}(n+10)u_n = r\sum_{n=1}^{\infty}(n+3)u_{n-1},$$
$$= r\sum_{n=0}^{\infty}(n+4)u_n,$$

and since $(n+10)u_n]_{n=0} = 10$, u_0 being 1,

therefore
$$\sum_{n=0}^{\infty}(n+10)u_n = r\sum_{n=0}^{\infty}(n+4)u_n + 10,$$

and
$$r(1-r)\frac{dS}{dr} + (10-4r)S = 10,$$

or
$$\frac{dS}{dr} + \frac{10-4r}{r(1-r)}S = \frac{10}{r(1-r)}.$$

Hence
$$S = e^{-\int\frac{10-4r}{r(1-r)}dr}\left[C + 10\int\frac{1}{r(1-r)}e^{\int\frac{10-4r}{r(1-r)}dr}\,dr\right]$$
$$= \frac{(1-r)^6}{r^{10}}\left[C + 10\int\frac{r^9}{(1-r)^7}\,dr\right].$$

To obtain
$$\int\frac{r^9}{(1-r)^7}dx, \quad \text{let } 1-r = x,$$

then
$$-\int\frac{(1-x)^9}{x^7}dx = \int\frac{(x-1)^9}{x^7}dx = \frac{x^3}{3} - \binom{9}{1}\frac{x^2}{2} + \binom{9}{2}x - \binom{9}{3}\log x - \binom{9}{4}\frac{1}{x}$$
$$+ \binom{9}{5}\frac{1}{2.x^2} - \binom{9}{6}\frac{1}{3x^3} + \binom{9}{7}\frac{1}{4.x^4} - \binom{9}{8}\frac{1}{5.x^5} + \frac{1}{6.x^6}.$$

Therefore
$$S = \frac{C(1-r)^6}{r^{10}} + \frac{10}{r^{10}}\left[\frac{(1-r)^9}{3} - \binom{9}{1}\frac{(1-r)^8}{2} + \binom{9}{2}(1-r)^7\right.$$
$$- \binom{9}{3}(1-r)^6\log(1-r) - \binom{9}{4}(1-r)^5 + \binom{9}{5}\frac{(1-r)^4}{2}$$
$$\left. - \binom{9}{6}\frac{(1-r)^3}{3} + \binom{9}{1}\frac{(1-r)^2}{4} - \binom{9}{8}\frac{1-r}{5} + \frac{1}{6}\right].$$

Multiplying by r^{10} and letting $r=0$, we have

$$C = 10\left[\frac{1}{3} - \binom{9}{1}\frac{1}{2} + \binom{9}{2} - \binom{9}{4} + \binom{9}{5}\frac{1}{2} - \binom{9}{6}\frac{1}{3} + \binom{9}{7}\frac{1}{4} - \binom{9}{8}\frac{1}{5} + \frac{1}{6}\right] = 0,$$

or $C = 518$.

Therefore

$$S = \frac{518(1-r)^6}{r^{10}} + \frac{10}{r^{10}}\left[\frac{(1-r)^9}{3} - \frac{9}{2}(1-r)^8 + 36(1-r)^7\right.$$
$$- 84(1-r)^6 \log(1-r) - 126(1-r)^5 + 63(1-r)^4$$
$$\left.- 28(1-r)^3 + 9(1-r)^2 - \frac{9}{5}(1-r) + \frac{1}{6}\right],$$
$$= \frac{840}{r^{10}}\left[-(1-r)^6 \log(1-r) - r - \frac{11}{12}r^2 - \frac{37}{3}r^3 + \frac{57}{4}r^4 - \frac{87}{10}r^5\right.$$
$$\left.+ \frac{49}{20}r^6 - \frac{1}{7}r^7 - \frac{1}{56}r^8 - \frac{1}{252}r^9\right].$$

IV. To find

$$S = \frac{a}{b} + \frac{a(a+1)}{b(b+1)}r + \frac{a(a+1)(a+2)}{b(b+1)(b+2)}r^2 + \ldots = \sum_{n=0}^{\infty} \frac{\prod\limits_{\kappa=0}^{n}(a+\kappa)}{\prod\limits_{\kappa=0}^{n}(b+\kappa)} r^n,$$

wherein a and b are positive integers and $a < b$.

$$\frac{\prod\limits_{\kappa=0}^{n}(a+\kappa)}{\prod\limits_{\kappa=0}^{n}(b+\kappa)} = \frac{(b-1)!\,(a+n)!}{(a-1)!\,(b+n)!} = \frac{(b-1)!}{(a-1)!}\frac{1}{\prod\limits_{\kappa=1}^{b-a}(n+a+\kappa)}.$$

Now

$$\frac{1}{\prod\limits_{\kappa=1}^{b-a}(n+a+\kappa)} = \sum_{\kappa=1}^{b-a}(-1)^{\kappa-1}\frac{(\kappa-1)!\,(b-a-1)!}{n+a+\kappa},$$

therefore

$$\frac{\prod\limits_{\kappa=0}^{n}(a+\kappa)}{\prod\limits_{\kappa=0}^{n}(b+\kappa)} = (b-a)\binom{b-1}{a-1}\sum_{\kappa=1}^{b-a}(-1)^{\kappa-1}\binom{b-a-1}{\kappa-1}\frac{1}{n+a+\kappa},$$

and

$$S = (b-a)\binom{b-1}{a-1}\sum_{\kappa=1}^{b-a}(-1)^{\kappa-1}\binom{b-a-1}{\kappa-1}\sum_{n=0}^{\infty}\frac{r^n}{n+a+\kappa},$$
$$= (b-a)\binom{b-1}{a-1}\sum_{\kappa=1}^{b-a}(-1)^{\kappa-1}\binom{b-a-1}{\kappa-1}\frac{1}{r^{a+\kappa}}\sum_{n=0}^{\infty}\frac{r^{n+a+\kappa}}{n+a+\kappa}.$$

Let $\sum\limits_{n=0}^{\infty} \dfrac{r^{n+a+\kappa}}{n+a+\kappa} = S_\kappa,$

then $\quad S_\kappa = \sum\limits_{n=a+\kappa}^{\infty} \dfrac{r^n}{n} = \sum\limits_{n=1}^{\infty} \dfrac{r^n}{n} - \sum\limits_{n=1}^{a+\kappa-1} \dfrac{r^n}{n}$

$$= -\log(1-r) - \sum\limits_{n=1}^{a+\kappa-1} \dfrac{r^n}{n},$$

and

$$S = (b-a)\binom{b-1}{a-1}\left[-\frac{\log(1-r)}{r^{a+1}} \sum\limits_{\kappa=0}^{b-a-1} (-1)^\kappa \binom{b-a-1}{\kappa} \frac{1}{r^\kappa} \right.$$
$$\left. + \frac{1}{r^a} \sum\limits_{\kappa=0}^{b-a} (-1)^\kappa \binom{b-a-1}{\kappa-1} \sum\limits_{n=1}^{a+\kappa-1} \frac{r^{n-\kappa}}{n} \right].$$

But

$$\sum\limits_{\kappa=0}^{b-a-1} (-1)^\kappa \binom{b-a-1}{\kappa} \frac{1}{r^\kappa} = \left(1 - \frac{1}{r}\right)^{b-a-1} = \frac{(r-1)^{b-a-1}}{r^{b-a-1}}.$$

Therefore

$$S = (b-a)\binom{b-1}{a-1}\left[\frac{(-1)^{b-a}\log(1-r)}{r^b}(1-r)^{b-a-1} \right.$$
$$\left. + \frac{1}{r^a} \sum\limits_{\kappa=1}^{b-a} (-1)^\kappa \binom{b-a-1}{\kappa-1} \sum\limits_{n=1}^{a+\kappa-1} \frac{r^{n-\kappa}}{n} \right].$$

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IX. *The Structure of Silver Crystals.*
By L. VEGARD, *Dr. phil., University of Christiania*[*].

AS a contribution to the study of the inner structure of crystals by the Röntgen ray analysis, I am going to give an account of the determination of the crystalline structure of silver.

Silver crystals belong to the cubic system, and are found in nature in very fine specimens of considerable size and with well-developed regular crystal-faces.

For the analysis I used the reflexion method of W. H. Bragg and W. L. Bragg [†], which is based on the determination of the reflexion angle of a homogeneous beam of X-rays.

The Röntgen-ray tube was of the sort recommended by Bragg, with a rhodium anticathode. The Röntgen-ray spectrometer was in principle the same as that constructed

[*] Communicated by the Author.
[†] W. H. Bragg and W. L. Bragg, Proc. Roy. Soc. A. vol. lxxxviii. p. 428.

by Bragg, although the particular arrangements were somewhat different. The slits and the ionization-chamber were mounted on the top of an ordinary Fuess goniometer, in such a way that the incident beam of X-rays and the axis of the ionization-chamber were parallel to the axes of the collimator and telescope respectively. The optical arrangements, however, were not removed, so the instrument could at the same time be used as a goniometer.

The crystal was mounted in the usual way on the crystal table with some wax. By means of a screw underneath the instrument the table could be moved up and down without any appreciable rotation of the crystal.

This arrangement proved very convenient, as it was possible to set the crystal-face very accurately by means of the optical arrangement, and then move it upwards until its central part came into level with the axis of the ionization-chamber.

The crystals used were two fine specimens which were kindly lent me by Professor W. C. Brögger, of the Mineralogical Laboratory. The one had the cube faces (100) and the other the tetrahedron faces (111) well developed.

The crystals were good reflectors. In order that no maximum might escape notice the entire ionization curve for varying angles was determined first with fairly wide slits (1 mm.). Then a more accurate measurement was made of the plate given by the strongest Rh line of wavelength $\lambda = 0 \cdot 607 \ 10^{-8}$ cm., using a slit about 0·4 mm. broad.

The condition for reflexion is given by the following formula of Bragg:

$$n\lambda = 2d \sin \theta;$$

d is the distance from one point plane to the next identical plane ; θ is the glancing angle of the incident beam, λ the wave-length, and n the order-number.

The zero position of the chamber, as determined from the direct beam, is perhaps less accurate than the position corresponding to maximum ionization from the reflected beam. From the position of the first and second maxima, however, we can easily calculate the true zero position and the true glancing angle θ.

Let the observed angles for the 1st, 2nd, &c. order be $\alpha_1, \alpha_2, \ldots$, and the true zero position α_0, then

$$\theta_1 = \frac{\alpha_1 - \alpha_0}{2}, \qquad \theta_2 = \frac{\alpha_2 - \alpha_0}{2}, \quad \text{and}$$

$$\cot 2\theta = 2 \operatorname{cosec} (\alpha_2 - \alpha_1) - \cot (\alpha_2 - \alpha_1).$$

For the reflexion planes (100) and (111), for which the crystal had corresponding crystal-faces, the maxima of 1st, 2nd, and 3rd order were found.   The calculation gave for α_0 the values $+1'$ and $-1'$ for the two faces respectively. Thus the fault in the direct determination of the zero position is practically negligible.

The crystal, however, had no marked (110) face, and to get the reflexion from these planes the cube-faced crystal was put up with the (110) plane vertical and the edge (100) horizontal.   But in this way the image of the reflected beam will not be a vertical slit, but will be ($>$) shaped, and the determination of the glancing angle less accurate.   Further, the reflexion from the (110) plane was so weak that only the first maximum could be measured.   But as the zero position is known, the first maximum will be sufficient for the determination of the glancing angle.

In fig. 1 is given the maxima corresponding to the strongest
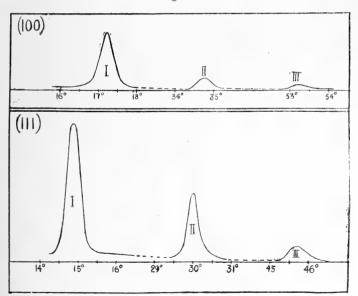
Fig. 1.

Rh line observed with the narrow slit, and in the table is given the glancing angle θ for the first order spectrum, the grating constant d, and the relative intensities of spectra of different orders.

Crystal plane.	θ_1.	d.	Relative Intensity.		
			1.	2.	3 order.
(100)	8° 36′	cm. $2\cdot030 \ 10^{-8}$	1·00	0·25	0·07
(110)	12° 11′	1·438 ,,		Not observed.	
(111)	7° 27′	2·341 ,,	1·00	0·49	0·10

The faces (100) and (111) show a normal·variation of intensities, with the intensity rapidly decreasing with increasing order.

For the ratio of the grating constants we get

$$\left.\begin{aligned}\frac{d_{111}}{d_{100}} &= 1\cdot1533 \\ \frac{2}{\sqrt{3}} &= 1\cdot1547\end{aligned}\right\} \frac{d_{111}}{d_{100}} = \frac{2}{\sqrt{3}}$$

$$\left.\begin{aligned}\frac{d_{110}}{d_{100}} &= 0\cdot7085 \\ \frac{1}{\sqrt{2}} &= 0\cdot7071\end{aligned}\right\} \frac{d_{110}}{d_{100}} = \frac{1}{\sqrt{2}}.$$

These are the well-known ratios, which belong to the face-centred cubic lattice * (fig. 2). For if the side of the smallest cube with one atom in each corner is $2a$, then we shall have

$$d_{100}=a, \quad d_{110}=\frac{a}{\sqrt{2}}, \quad d_{111}=\frac{2a}{\sqrt{3}}.$$

Thus the ratios of the grating constants are explained from the face-centred lattice. This arrangement would further explain the normal distribution of intensities, as all point planes parallel to one of the faces examined should be identical and equidistant.

To put the lattice to a final test we shall calculate from observations the number (n) of atoms which are associated with a cube of side d_{100}.
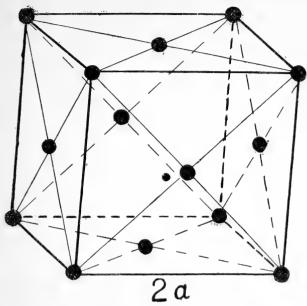
In the volume of the whole cube lattice with side $2a$ (fig. 2) there are 4 atoms, and in the cube with a side $a=d_{100}$ there should be $\frac{1}{2}$ atom on an average.

For the number n we get

$$n = \frac{\rho}{A} N d_{100}^3.$$

* W. H. Bragg and W. L. Bragg, Proc. Roy. Soc. vol. lxxxix. p. 281.

Fig. 2.

$2a$

ρ is the density of silver (10·50) and A the atomic weight (107·93). N is the number of atoms in a gramme equivalent ($61·5 \times 10^{22}$), and d_{100} is given in the table. Inserting these values,

$$n = 0·50002, \text{ or } \tfrac{1}{2}.$$

Thus the face-centred cubic lattice explains the whole series of experiments, and we come to the conclusion *that the atoms in the silver crystals are arranged in the simple face-centred lattice.*

The arrangement is the same as that previously found by W. L. Bragg for copper crystals [*].

In conclusion, I wish to thank Professor W. H. Bragg and Mr. W. L. Bragg for valuable information with regard to the methods of the crystal analysis, Professor W. C. Brögger for his kindness in lending me the crystals and the goniometer on which the Röntgen-ray spectrometer was mounted, and Professor V. Goldschmidt for helpful advice with regard to crystal work in general. Finally, my thanks are due to Mr. Harald K. Schjelderup for his assistance in making the readings.

Christiania, Oct. 20, 1915.

* W. L. Bragg, " On the Crystalline Structure of Copper," Phil. Mag. vol xxviii. p. 355 (1914).

X. *Notices respecting New Books.*

Functions of a Complex Variable. Professor JAMES PIERPONT.
Ginn & Co. 20*s.* net.

THIS volume deals with the elementary parts of the theory of functions of a complex variable, and is the outcome of lectures given over a considerable number of years to students of Yale University.

The opening chapters give an account of the exponential, circular, hyberbolic, and other functions, followed by the consideration of differentiation and integration, the general properties of analytic functions, infinite products, and asymptotic series, in the latter case with reference to Gamma and Bessel functions.

To illustrate the general principles of the theory, a brief treatment is given of the elliptic functions, more particularly from the standpoint of their most characteristic property of double periodicity. The final chapters, devoted to linear differential equations, the functions of Legendre, Laplace, Bessel, and Lamé, with their more important properties, will appeal especially to the student of mathematical physics.

Professor Pierpont's style is clear and simple and his treatment sound and thorough. The book can be heartily recommended to students who need a work in which the principles of the function theory are carefully presented. It will serve as a useful introduction to the subject, and will, no doubt, arouse the interest of students and induce them to read the more advanced treatises and original memoirs mentioned in the text. Even the private student, who has not the advantage of a teacher's assistance in overcoming his difficulties, should find the book particularly helpful.

XI. *Intelligence and Miscellaneous Articles.*

ON THE STRUCTURE OF THE SPINEL GROUP OF CRYSTALS.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—
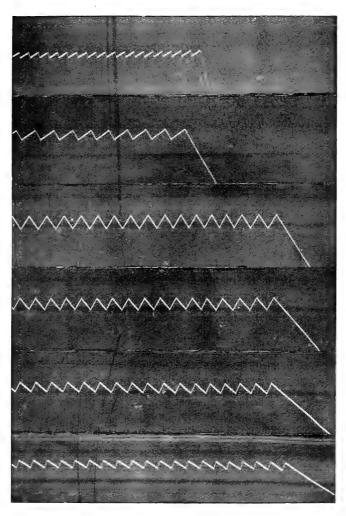
I HAVE recently received from Mr. S. Nishikawa a copy of a paper which he contributed last December to the Proceedings of the "Tokyo Mathematico-Physical Society." It deals with the structure of the spinel group of crystals. In August last you were good enough to publish an account of some experiments of my own on the same subject. I need hardly say that if I had known of Mr. Nishikawa's work I should not have written my paper without referring to it.

I am very glad to find that though our methods were entirely different there is no disagreement between our results.

Yours &c.

Dec. 15, 1915. W. H. BRAGG,

Photographs showing the initial movement and the subsequent
vibration with discontinuous changes of velocity.

XII. *On the Propagation of Sound in narrow Tubes of variable section.* By Lord RAYLEIGH, *O.M., F.R.S.*[*]

UNDER this head there are two opposite extreme cases fairly amenable to analytical treatment, (i.) when the changes of section are so slow that but little alteration occurs within a wave-length of the sound propagated and (ii.) when any change that may occur is complete within a distance small in comparison with a wave-length.

In the first case we suppose the tube to be of revolution. A very similar analysis would apply to the corresponding problem in two dimensions, but this is of less interest. If the velocity-potential ϕ of the simple sound be proportional to e^{ikat}, the equation governing ϕ is

$$\frac{d^2\phi}{dr^2} + \frac{1}{r}\frac{d\phi}{dr} + \frac{d^2\phi}{dx^2} + k^2\phi = 0, \quad . \quad . \quad . \quad (1)$$

where x is measured along the axis of symmetry and r perpendicular to it. Since there are no *sources* of sound along the axis, the appropriate solution is [†]

$$\phi = J_0\{r\sqrt{(d^2/dx^2 + k^2)}\}F(x), \quad . \quad . \quad . \quad (2)$$

in which F, a function of x only, is the value of ϕ when $r = 0$.

At the wall of the tube $r = y$, a known function of x; and the boundary condition, that the motion shall there be tangential, is expressed by

$$- \frac{d\phi}{dx}\frac{dy}{dx} + \frac{d\phi}{dr} = 0, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which $(r = y)$

$$\frac{d\phi}{dx} = \frac{d\mathrm{F}}{dx} - \frac{y^2}{2^2}\left(\frac{d^2}{dx^2} + k^2\right)\frac{d\mathrm{F}}{dx} + \frac{y^4}{2^2.4^2}\left(\frac{d^2}{dx^2} + k^2\right)^2\frac{d\mathrm{F}}{dx} - \ldots, \quad . \quad (4)$$

$$\frac{d\phi}{dr} = -\frac{y}{2}\left(\frac{d^2}{dx^2} + k^2\right)\mathrm{F} + \frac{y^3}{2^2.4}\left(\frac{d^2}{dx^2} + k^2\right)^2\mathrm{F} - \ldots. \quad . \quad . \quad (5)$$

Using these in (3), we obtain an equation which may be put into the form

$$\frac{d^2}{dx^2}(y\mathrm{F}) + k^2(y\mathrm{F}) = \frac{d^2y}{dx^2}\mathrm{F} + \frac{y^2}{2}\frac{dy}{dx}\left(\frac{d^2}{dx^2} + k^2\right)\frac{d\mathrm{F}}{dx}$$

$$- \frac{y^4}{32}\frac{dy}{dx}\left(\frac{d^2}{dx^2} + k^2\right)^2\frac{d\mathrm{F}}{dx} + \ldots + \frac{y^3}{8}\left(\frac{d^2}{dx^2} + k^2\right)^2\mathrm{F} - \ldots. \quad . \quad (6)$$

As a first approximation we may neglect all the terms on the right of (6), so that the solution is

$$\mathrm{F}(x) = \frac{\mathrm{A}e^{-ikx} + \mathrm{B}e^{ikx}}{y}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where A and B are constants. To the same approximation,

$$\frac{d^2\mathrm{F}}{dx^2} + k^2\mathrm{F} = -\frac{2}{y}\frac{dy}{dx}\frac{d\mathrm{F}}{dx}. \quad . \quad . \quad . \quad . \quad (8)$$

For a second approximation we retain on the right of (6) all terms of the order d^2y/dx^2, or $(dy/dx)^2$. By means of (8) we find sufficiently for our purpose

$$\left(\frac{d^2}{dx^2} + k^2\right)\frac{d\mathrm{F}}{dx} = -\frac{2}{y}\frac{dy}{dx}\frac{d^2\mathrm{F}}{dx^2},$$

$$\left(\frac{d^2}{dx^2} + k^2\right)^2\mathrm{F} = 4\frac{d^2\mathrm{F}}{dx^2}\left\{\frac{2}{y^2}\left(\frac{dy}{dx}\right)^2 - \frac{1}{y}\frac{d^2y}{dx^2}\right\},$$

$$\left(\frac{d^2}{dx^2} + k^2\right)^2\frac{d\mathrm{F}}{dx} = 0, \quad \left(\frac{d^2}{dx^2} + k^2\right)^4\mathrm{F} = 0.$$

Our equation thus becomes

$$\left(\frac{d^2}{dx^2} + k^2\right)(y\mathrm{F}) = \frac{d^2y}{dx^2}\,\mathrm{F} - \frac{y^2}{2}\,\frac{d^2y}{dx^2}\,\frac{d^2\mathrm{F}}{dx^2}$$

$$= (1 + \tfrac{1}{2}k^2y^2)\,\frac{d^2y}{dx^2}\cdot\mathrm{F}(x), \quad . \quad . \quad (9)$$

in which on the right the first approximation (7) suffices. Thus

$$y\mathrm{F}(x) = \frac{1}{2ik}\left\{ e^{ikx}\int \mathrm{Y}(\mathrm{B} + \mathrm{A}e^{-2ikx})\,dx \right.$$

$$\left. - e^{-ikx}\int \mathrm{Y}(\mathrm{A} + \mathrm{B}e^{2ikx})\,dx \right\}, \quad . \quad . \quad (10)$$

where

$$\mathrm{Y} = \frac{1 + \tfrac{1}{2}k^2y^2}{y}\,\frac{d^2y}{dx^2}. \quad . \quad . \quad . \quad . \quad (11)$$

In (10) the lower limit of the integrals is undetermined ; if we introduce arbitrary constants, we may take the integration from $-\infty$ to x.

In order to attack a more definite problem, let us suppose that d^2y/dx^2, and therefore Y, vanishes everywhere except over the finite range from $x=0$ to $x=b$, b being positive. When x is negative the integrals disappear, only the arbitrary constants remaining ; and when x is positive the integrals may be taken from 0 to x. As regards the values of the constants of integration, (10) may be supposed to identify itself with (7) on the negative side. Thus

$$y\mathrm{F}(x) = e^{-ikx}\left\{ \mathrm{A} - \frac{1}{2ik}\int_0^x \mathrm{Y}(\mathrm{A} + \mathrm{B}e^{2ikx})\,dx \right\}$$

$$+ e^{ikx}\left\{ \mathrm{B} + \frac{1}{2ik}\int_0^x \mathrm{Y}(\mathrm{B} + \mathrm{A}e^{-2ikx})\,dx \right\}. \quad (12)$$

The integrals disappear when x is negative, and when x exceeds b they assume constant values.

Let us now further suppose that when x exceeds b there is no negative wave, *i. e.* no wave travelling in the negative direction. The negative wave on the negative side may then be regarded as the *reflexion* of the there travelling positive wave. The condition is

$$\mathrm{B}\left\{ 1 + \frac{1}{2ik}\int_0^b \mathrm{Y}\,dx \right\} + \frac{\mathrm{A}}{2ik}\int_0^b \mathrm{Y}e^{-2ikx}\,dx = 0, \quad (13)$$

giving the reflected wave (B) in terms of the incident

wave (A). There is no reflexion if

$$\int_0^b Y e^{-2ikx} dx = 0 ; \quad . \quad . \quad . \quad . \quad (14)$$

and then the transmitted wave $(x > b)$ is given by

$$F(x) = \frac{A e^{-ikx}}{y} \left\{ 1 - \frac{1}{2ik} \int_0^b Y dx \right\}. \quad . \quad . \quad . \quad (15)$$

Even when there is reflexion, it is at most of the second order of smallness, since Y is of that order. For the transmitted wave our equations give $(x > b)$

$$F(x) = \frac{A e^{-ikx}}{y} \left\{ 1 - \frac{1}{2ik} \int_0^b Y dx \right.$$

$$\left. - \frac{1}{4k^2} \frac{\int_0^b Y e^{-2ikx} dx \cdot \int_0^b Y e^{2ikx} dx}{1 + \frac{1}{2ik} \int_0^b Y dx} \right\} ; \quad . \quad (16)$$

but if we stop at the second order of smallness the last part is to be omitted, and (16) reduces to (12). It appears that to this order of approximation the intensity of the transmitted sound is equal to that of the incident sound, at least if the tube recovers its original diameter. If the final value of y differs from the initial value, the intensity is changed so as to secure an equal propagation of energy.

The effect of Y in (15) is upon the *phase* of the transmitted wave. It appears, rather unexpectedly, that there is a linear *acceleration* amounting to

$$\frac{1}{2k^2} \int_0^b Y dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

or, since the ends of the disturbed region at 0 and b are cylindrical,

$$\frac{1}{2k^2} \int_0^b \frac{1}{y^2} \left(\frac{dy}{dx} \right)^2 (1 - \tfrac{1}{2} k^2 y^2) dx, \quad . \quad . \quad . \quad (18)$$

from which the term in $k^2 y^2$ may be dropped.

That the reflected wave should be very small when the changes are sufficiently gradual is what might have been expected. We may take (13) in the form

$$\frac{B}{A} = \frac{i}{2k} \int_0^b Y e^{-2ikx} dx = \frac{i}{2k} \int_0^b \frac{1}{y} \frac{d^2 y}{dx^2} e^{-2ikx} dx. \quad . \quad . \quad (19)$$

As an example let us suppose that from $x=0$ to $x=b$
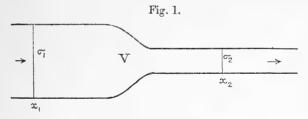
$$y = y_0 + \eta(1 - \cos mx), \quad . \quad . \quad . \quad (20)$$

where y_0 is the constant value of y outside the region of disturbance, and $m = 2\pi/b$. If we suppose further that η is small, we may remove $1/y$ from under the sign of integration, so that

$$\frac{B}{A} = \frac{im^2\eta}{2ky_0} \int_0^b \cos mx\, e^{-2ikx} dx$$

$$= \frac{m^2\eta}{4k^2 y_0} \{1 - \cos 2kb + i \sin 2kb\}. \quad . \quad . \quad (21)$$

Independently of the last factor (which may vanish in certain cases) B is very small in virtue of the factors m^2/k^2 and η/y_0.

In the second problem proposed we consider the passage of waves proceeding in the positive direction through a tube (not necessarily of revolution) of uniform section σ_1 and impinging on a region of irregularity, whose length is small compared with the wave-length (λ). Beyond this region the tube again becomes regular of section σ_2 (fig. 1).

Fig. 1.

It is convenient to imagine the axes of the initial and final portions to be coincident, but our principal results will remain valid even when the irregularity includes a bend. We seek to determine the transmitted and reflected waves as proportional to the given incident wave.

The velocity-potentials of the incident and reflected waves on the left of the irregularity and of the transmitted wave on the right are represented respectively by

$$\phi_1 = Ae^{-ikx} + Be^{ikx}, \quad \phi_2 = Ce^{-ikx}; \quad . \quad . \quad . \quad (22)$$

so that at x_1 and x_2 we have

$$\phi_1 = Ae^{-ikx_1} + Be^{ikx_1}, \qquad \phi_2 = Ce^{-ikx_2}, \quad . \quad . \quad (23)$$

$$d\phi_1/dx = ik(-Ae^{-ikx_1} + Be^{ikx_1}), \quad d\phi_2/dx = -ikCe^{-ikx_2}. \quad (24)$$

When λ is sufficiently great we may ignore altogether the space between x_1 and x_2, that is we may suppose that the pressures are the same at these two places and that the total flow is also the same, as if the fluid were incompressible. As there is now no need to distinguish between x_1 and x_2, we may as well suppose both to be zero. The condition $\phi_1 = \phi_2$ gives

$$A + B = C, \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

and the condition $\sigma_1 d\phi_1/dx = \sigma_2 d\phi_2/dx$ gives

$$\sigma_1(-A + B) = -\sigma_2 C. \quad . \quad . \quad . \quad . \quad (26)$$

Thus
$$\frac{B}{A} = \frac{\sigma_1 - \sigma_2}{\sigma_1 + \sigma_2}, \qquad \frac{C}{A} = \frac{2\sigma_1}{\sigma_1 + \sigma_2}. \quad . \quad . \quad . \quad (27)$$

These are Poisson's formulæ[*]. If σ_1 and σ_2 are equal, we have of course $B = 0$, $C = A$. Our task is now to proceed to a closer approximation, still supposing that the region of irregularity is small.

For this purpose both of the conditions just now employed need correction. Since the volume V of the irregular region is to be regarded as sensible and the fluid is really susceptible of condensation (s), we have

$$V\frac{ds}{dt} = \sigma_1 \frac{d\phi_1}{dx_1} - \sigma_2 \frac{d\phi_2}{dx_2},$$

and since in general $s = -a^{-2} d\phi/dt$, we may take

$$\frac{ds}{dt} = -a^{-2}\frac{d\phi_1}{dt^2} \quad \text{or} \quad -a^{-2}\frac{d^2\phi_2}{dt^2},$$

the distinction being negligible in this approximation in virtue of the smallness of V. Thus

$$\sigma_1 \frac{d\phi_1}{dx_1} - \sigma_2 \frac{d\phi_2}{dx_2} = -\frac{V}{a^2}\frac{d^2\phi_2}{dt_2} = k^2 V \phi_2. \quad . \quad . \quad (28)$$

In like manner, assimilating the flow to that of an incompressible fluid, we have for the second condition

$$\phi_2 - \phi_1 = R\sigma_2 \frac{d\phi_2}{dx_2}, \quad . \quad . \quad . \quad . \quad (29)$$

where R may be defined in electrical language as the *resistance* between x_1 and x_2, when the material supposed to be bounded by non-conducting walls coincident with the walls of the tube is of unit specific resistance.

---

[*] Compare 'Theory of Sound,' § 264.

In substituting the values of ϕ and $d\phi/dx$ from (23), (24) it will shorten our expressions if for the time we merge the exponentials in the constants, writing

$$A' = Ae^{-ikx_1}, \quad B' = Be^{ikx_1}, \quad C' = Ce^{-ikx_2}. \quad . \quad (30)$$

Thus
$$\sigma_1(-A' + B') + \sigma_2 C' = -ikVC', \quad . \quad . \quad . \quad (31)$$

$$A' + B' - C' = ik\sigma_2 RC'. \quad . \quad . \quad . \quad (32)$$

We may check these equations by applying them to the case where there is really no break in the regularity of the tube, so that

$$\sigma_1 = \sigma_2, \quad V = (x_2 - x_1)\sigma, \quad R = (x_2 - x_1)/\sigma.$$

Then (31), (32) give $B' = 0$, or $B = 0$, and

$$\frac{C'}{A'} = \frac{1}{1 + ik(x_2 - x_1)} = e^{-ik(x_2 - x_1)},$$

with sufficient approximation. Thus

$$C'e^{ikx_2} = A'e^{ikx_1}, \quad \text{or} \quad C = A.$$

The undisturbed propagation of the waves is thus verified.

In general,

$$\frac{B'}{A'} = \frac{\sigma_1 - \sigma_2 + ik(\sigma_1\sigma_2 R - V)}{\sigma_1 + \sigma_2 + ik(\sigma_1\sigma_2 R + V)}, \quad . \quad . \quad . \quad (33)$$

$$\frac{C'}{A'} = \frac{2\sigma_1}{\sigma_1 + \sigma_2 + ik(\sigma_1\sigma_2 R + V)}. \quad . \quad . \quad . \quad (34)$$

When $\sigma_1 - \sigma_2$ is finite, the effect of the new terms is only upon the phases of the reflected and transmitted waves. In order to investigate changes of intensity we should need to consider terms of still higher order.

When $\sigma_1 = \sigma_2$, we have

$$C' = A' \left\{ 1 - \frac{ik}{2\sigma}(\sigma^2 R + V) \right\} = A'e^{-ik(\sigma^2 R + V)/2\sigma},$$

$$C = Ae^{ik(x_2 - x_1 - \frac{1}{2}\sigma R - V/2\sigma)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

making, as before, $C = A$, if there be no interruption. Also, when $\sigma_1 = \sigma_2$ absolutely,

$$\frac{B'}{A'} = \frac{ik(\sigma^2 R - V)}{2\sigma}, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

indicating a change of phase of $90°$, and an intensity referred to that of the incident waves equal to

$$\frac{k^2(\sigma^2 R - V)^2}{4\sigma^2}. \quad . \quad . \quad . \quad . \quad (37)$$

As an example let us take the case of a tube of revolution for which y, being equal to y_0 over the regular part, becomes $y_0 + \delta y$ between x_1 and x_2.   We have

$$\frac{V}{2\sigma} = \frac{1}{2}(x_2 - x_1) + \int \frac{\delta y}{y_0} dx + \frac{1}{2} \int \left(\frac{\delta y}{y_0}\right)^2 dx.$$

Also *

$$\frac{1}{2}\sigma R = \frac{1}{2}y_0^2 \int \frac{dx}{y^2}\left\{ 1 + \frac{1}{2}\left(\frac{dy}{dx}\right)^2\right\} dx$$

$$= \frac{1}{2}(x_2 - x_1) - \int \frac{\delta y}{y_0} dx + \frac{3}{2}\int\left(\frac{\delta y}{y_0}\right)^2 dx + \frac{1}{4}\int\left(\frac{d\delta y}{dx}\right)^2 dx,$$

and

$$\frac{V}{2\sigma} + \frac{\sigma R}{2} = (x_2 - x_1) + \int_{x_1}^{x_2}\left\{ 2\left(\frac{\delta y}{y_0}\right)^2 + \frac{1}{4}\left(\frac{d\delta y}{dx}\right)^2\right\} dx, \quad . \quad (38)$$

the terms of the first order in δy disappearing. Thus in the exponent of (35)

$$x_2 - x_1 - \tfrac{1}{2}\sigma R - V/2\sigma = -\int\left\{ 2(\delta y/y_0)^2 + \tfrac{1}{4}(d\delta y/dx)^2\right\} dx,$$
$$\quad . \quad . \quad (39)$$

of which the right hand member, taken with the positive sign, expresses the retardation of the transmitted wave due to the departure from regularity.

XIII. *The Wave-length of the Electrical Vibration associated with a thin Straight terminated Conductor.   By* J. A. Pollock, *D.Sc., Professor of Physics in the University of Sydney* †.

TO a first approximation, Abraham ‡ and other writers conclude from theoretical considerations that the wave-length of the disturbance in free æther due to the gravest electrical vibration on a thin straight terminated conductor is equal to twice the length of the rod.   This result is very definitely supported by Lord Rayleigh § in opposition to the calculation of Macdonald ||, which makes the wave-length $2 \cdot 53$ times the length of the conductor.

    * 'Theory of Sound,' § 308.
    † Communicated by the Author.   Read before the Royal Society of N. S. Wales.
    ‡ Abraham, *Ann. der Physik,* xlvi. p. 435 (1898).
    § Rayleigh, Phil. Mag. viii. p. 105 (1904): Phil. Mag. xxv. p. 1 (1913).
    || Macdonald, 'Electric Waves,' p. 111 (1902).

Some years ago I published an account * of an experimental comparison, by a resonance method, of the periods of the electrical vibrations associated with simple circuits.   In discussing the results, I assumed that the wave-length of the oscillation connected with a narrow rectangular circuit was equal to the perimeter of the rectangle, and was led to think that the measurements supported Macdonald's theoretical deduction as to the wave-length of the vibration on a straight rod.   The assumption, which affects the discussion only, is, however, quite unjustifiable, as the wave-length depends on the ratio of length to breadth as well as on the perimeter of the circuit.   Contrary to the opinion I then expressed, the experimental results cannot be taken as supporting Macdonald's theory.

More recently, several values of the ratio of wave-length to length of conductor, determined from interference experiments, have been given in accounts of measurements of electric waves from linear oscillators of small dimensions. Writing $\lambda = kl$, where l is the length of the conductor, Willard and Woodman† deduce for k the value 2·48; Cole‡, 2·52; Blake and Fountain§, 2·47; and Webb and Woodman ‖, 2·3.   Finally, Ives¶, using a very high resistance receiver with an interferometer arrangement, finds 2·04 as the value of k for certain linear oscillators varying in length from 5 to 10 centimetres.

At the meeting of the British Association in Sydney, in 1914, I mentioned that the interference experiments had recently been repeated by students in the Physical Laboratory of the University, with results completely confirming those of Ives.   I now give a summary of the measurements.

In the interferometer experiments Ives' general arrangement has been followed, but a coherer was used as a receiver instead of one involving a thermo-electric junction.   At each observation the coherer was isolated during the passage of the waves, being connected to the galvanometer circuit, by movable conductors working in mercury cups, only after sparking had ceased.   A coherer used in this way is unaffected by disturbances not in its immediate neighbourhood.

The positions of the nodes of the stationary wave system, formed by the reflexion of an incident beam at a plane zinc

* Pollock, Journ. and Proc. Roy. Soc. N. S. Wales, xxxvii. p. 198 (1903); Phil. Mag. vii. p. 635 (1904).
† Willard and Woodman, Phys. Rev. xviii. p. 1 (1904).
‡ Cole, Phys. Rev. xx. p. 268 (1905).
§ Blake and Fountain, Phys. Rev. xxiii. p. 256 (1906).
‖ Webb and Woodman, Phys. Rev. xxix. p. 89 (1909).
¶ Ives, Phys. Rev. xxx. p. 199 (1910); xxxi. p. 185 (1910).

mirror, have also been determined with the same coherer arrangement. The results exactly agree with those found with the interferometer.

For these and the interferometer measurements, the oscillator, sparking in paraffin, was placed at the focus of a cylindrical parabolic mirror, the focal length being an odd multiple of a quarter of the wave-length to be expected. Experiments have been made with mirrors whose focal lengths were calculated from the lengths of the oscillators on the basis of both Abraham's and Macdonald's theories. Ives' conclusion that the focal length of the oscillator mirror has a negligible effect on the wave-length has been verified.

The various values which have been found are set out in the following table, together with the names of the experimenters who carried out the considerable practical work involved in the determinations. To make the evidence complete, I have included the results of Ives' measurements. The other measures, previously mentioned, are not given in the table, as the earlier experiments are open to the criticism that the influence of the receivers was not entirely eliminated. Ives' use of a very high resistance in the receiver circuit quite obviates an error of this kind. In the experiments in this laboratory, coherers of very dissimilar dimensions were employed in verifying the results, and it was definitely proved that the measurements were wholly independent of any characteristic of the receiving circuits.

Experimenters.	Length of Oscillator.	λ obs.	λ calc.	k obs.	k calc.	Experimental Method.	Number of nodes determined.	Approximate distance from plane mirror.
[1] Ives	4·93	10·42	10·12	2·11	2·05	Interferometer.		
	7·49	15·24	15·30	2·03	2·04	,,		
	9·85	19·86	20·06	2·02	2·04	,,		
[2] Booth & Tiddy	5·06	10·40	10·30	2·06	2·06	,,	3	
,, ,,	,,	10·54	,,	2·08	,,	Stationary Waves.	4	100 λ
,, ,,	,,	10·46	,,	2·07	,,	,,	4	,,
,, ,,	,,	10·40	,,	2·06	,,	,,	3	5 λ
,, ,,	18·84	38·47	38·38	2·05	2·03	,,	11	20 λ
[3] Anderson & Scarr.	,,	38·00	,,	2·01	,,	,,	5	5 λ

[1] Ives, *loc. cit.*   [2] E. H. Booth, H. P. Tiddy.
[3] R. C. Anderson, J. H. A. Scarr.

In his theoretical discussion of this subject Abraham *
considers the vibration about a perfect conductor in the form
of an elongated ellipsoid of revolution. When the minor
axis (2 *b*) becomes negligibly small in comparison with the
major axis (*l*), the wave-length in free æther of the disturb-
ance due to the fundamental vibration is equal to 2*l*. In
a second approximation Abraham obtains the following
expression for this wave-length :—

$$\lambda = 2l \left(1 + 5 \cdot 6 \epsilon^2\right)$$

where $1/\epsilon = 4 \log_e (l/b)$.

In the table, under the heading "λ calculated," are given
the wave-lengths deduced from this equation, and under
"*k* calculated," the ratio of these wave-lengths to the lengths
of the oscillators.

A consideration of the evidence shows that Abraham's
expression gives a result for the wave-length which agrees
with the measured value within the present limits of experi-
mental error. This was Ives' conclusion in 1910, and the
results now published add to his statement but the weight
attached to confirmation from independent work. The
physical accuracy of Abraham's deduction is now sufficiently
well established for linear oscillators of known dimensions to
be used as standards in connexion with the measurement of
short electric waves.

These results completely support Lord Rayleigh's † view
of the value of the wave-length of the vibration on a thin
straight terminated rod, and at least imply the experimental
verification of his contention "that the difference between
the half wave-length of the gravest vibration and the
length (*l*) of the rod (of uniform section) tends to vanish
relatively when the section is reduced without limit."

The experiments lend no support to Macdonald's calcu-
lation, which requires that the numbers in the table under
the heading "*k* observed" should be 2·5. It would appear,
then, that Sarasin and De la Rive's well-known experiments
which, hitherto, have only been quantitatively described in
terms of Macdonald's theory, still await their explanation.

The University of Sydney,
September 24th, 1915.

* Abraham, *loc. cit.*
† Rayleigh, *loc. cit.*

XIV. *On the Velocities of the Electrons emitted in the Normal and Selective Photo-Electric Effects. By* A. Ll. Hughes, *D.Sc., B.A., Assistant Professor of Physics at the Rice Institute, Houston, Texas* *.

THERE is a marked difference between the photo-electric effect in the alkali metals and that in other metals. When polarized light falls upon a polished metal, such as platinum or copper, the number of electrons emitted per unit energy of the incident light increases rapidly as the wavelength decreases. The emission of electrons is somewhat greater when the light is polarized in the E‖ plane than when it is polarized in the E⊥ plane †. This, however, is fully accounted for by the fact that when light is polarized in the E‖ plane, more light is absorbed than when the light is polarized in the E⊥ plane ‡. So, if we measure the number of electrons emitted per unit energy of absorbed light, the photo-electric effect does not depend upon the state of polarization of the light. With the alkali metals, however, the case is very different. Many more electrons are emitted when the light is polarized in the E‖ plane than when it is polarized in the E⊥ plane. The typical relation between the photo-electric current from an alkali metal illuminated by polarized monochromatic light and the state of polarization is shown in fig. 1. Pohl and Pringsheim § distinguish between two kinds of photo-electric effect, the "normal effect" and the "selective effect." The selective effect is shown only by the alkali metals, and then only when the light is polarized in the E‖ plane and limited to a certain range of wave-lengths. The selective effect is the abnormally great photo-electric effect obtained with light (limited to a certain range of wave-lengths) polarized in the E‖ plane. The number of electrons emitted with light of the wavelength at which the selective effect is a maximum may be from 20 to 300 times as great as the normal effect for the same wave-length. With unpolarized light of this wavelength, the photo-electric current is mainly due to the electrons emitted in the selective effect. Pohl and Pringsheim

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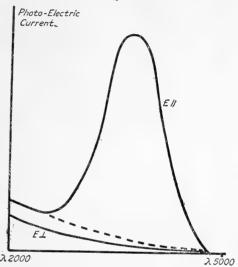
† We shall refer to the plane of polarization parallel to the plane of incidence as the E‖ plane, and to the plane of polarization at right angles to this as the E⊥ plane. In terms of the Electromagnetic Theory of Light, E denotes the electric force and the sign after it denotes the relation of the force to the plane of incidence.

‡ Pohl, *Verh. d. Deutsch. Phys. Ges.* x. pp. 339, 609, 715 (1909).

§ Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xii. p. 215 (1910).

believe that the selective and normal effects have their origin in two independent processes. If this were so, one would expect that the electrons emitted in the selective effect and in the normal effect would have quite different velocities and

Fig. 1.

distributions of velocities. The indirect evidence bearing on this point, however, suggests that there is practically no difference between the velocities of emission in the two effects. Certain definite laws have been established as to the relation between the maximum emission velocity and distribution of velocities on the one hand, and the wavelength on the other. These laws have been found from experiments on metals outside the alkali group. But Richardson and Compton *, Kadesch †, and Millikan ‡ have included in their work experiments on sodium, and it is significant that there is nothing abnormal in the results for sodium. It has already been mentioned that, with unpolarized light, the majority of the electrons emitted from an alkali metal are those associated with the selective effect. The evidence from these experiments, therefore, does not point to any appreciable difference between the two effects so far as we can judge from velocities. It should be mentioned that Elster and Geitel § record an observation in the course
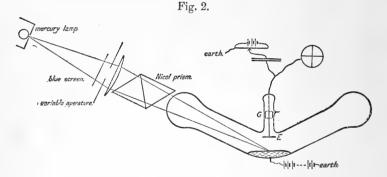
* Richardson and Compton, Phil. Mag. xxiv. p. 576 (1912).
† Kadesch, Phys. Rev. iii. p. 367 (1914).
‡ Millikan, Phys. Rev. iv. p. 73 (1914).
§ Elster and Geitel, *Phys. Zeits.* . 457 (1909).

of a research on the selective effect which would seem to show that the electrons emitted in the selective effect were on the whole somewhat slower than those emitted in the normal effect.
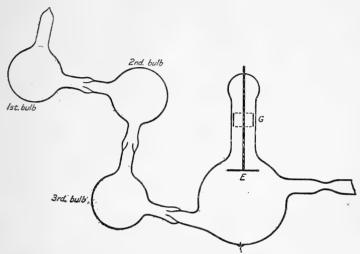
It was therefore thought desirable to investigate the velocities of the electrons emitted in the selective and normal effects. As the evidence available tends to show that the distribution of velocities of the electrons is the same in both cases, the apparatus was designed to show whether this was true or not. To find out exactly the nature of the difference (if any) in the distribution of velocities would require a more complicated apparatus. It is highly desirable when working with sodium-potassium alloy, which is so sensitive to traces of reacting gases, to keep the apparatus as simple as possible.

The apparatus consisted of a bent glass tube about 3 cm. wide (fig. 2). The inside was plated with a semi-transparent

Fig. 2.

film of platinum except for the rounded ends which acted as windows. A guard-ring G served to prevent any electrification from leaking over the glass from the platinized surface to the electrode E. Sealing-wax around the outside of the platinum seal making connexion with the electrode E gave satisfactory insulation. The sodium-potassium alloy was strongly heated before being put into the apparatus to drive off occluded gases. It was then placed in the first bulb connected with the apparatus (fig. 3), which was exhausted by means of a Gaede mercury-pump and charcoal cooled by liquid air. The apparatus was strongly heated for several hours while the exhaustion proceeded, and then, by suitably tilting the apparatus, the alloy was filtered from the first bulb into the second. The alloy was heated for several hours again and then transferred to the third bulb. The apparatus was now sealed off from the pump and allowed to

stand for two days, after which the alloy was finally transferred to the bottom of the wide tube where it was to be illuminated.

Fig. 3.

The light was given by a mercury lamp. A Wratten blue filter was used to limit the light to the wave-lengths $\lambda 4360$ and $\lambda 4050$, where the selective effect is near its maximum for sodium-potassium alloy. The image of a small aperture in a sheet of metal close to the mercury lamp was focussed on the surface of the alloy just under the electrode E. The image formed a spot of light about 4 mm. square, which did not shift more than 1 mm. on rotating the Nicol prism. The amount of light received by the alloy could be altered by varying the aperture of the lens without altering the dimensions of the patch of light on the surface of the alloy.

The charge received by the electrode E was measured by a null method. The plate of a condenser of capacity 250 cm. was connected to the same quadrant of an electrometer as E. The potential on the other plate was altered at such a rate as to keep the needle of the electrometer undeflected. If the potential on the condenser has to be altered at the rate of V volts in a time t, the photo-electric current received by E is

$$i = \frac{CV}{t},$$

where C is the capacity of the condenser.

The method of experiment was as follows:—When there is no field between the alloy and E, the electrons leave the illuminated surface in straight lines in all directions. When a field is established, the paths of the electrons are curved more or less towards the electrode E which now receives a greater current. A sufficiently large field will pull all the electrons into E. The number reaching E is a function (1) of the potential difference between it and the alloy, and (2) of the velocity and direction of emission of the electrons. There are two distributions of electrons to consider, a *direction distribution* and a *velocity distribution*. If the photo-electrons liberated in the selective effect and those liberated in the normal effect had identical velocity distributions and direction distributions, then one would obtain exactly similar curves connecting the charge received by the electrode E and the potential applied to the alloy.
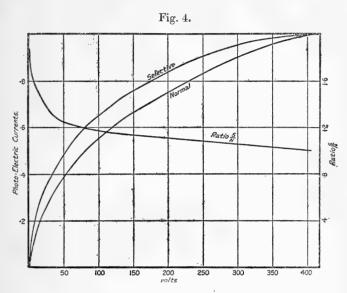
The current obtained with an accelerating potential of 404 volts is arbitrarily taken to be equal to unity, for both effects. The results are given in Table I. Some experiments

TABLE I.

Accelerating potential.	Photo-electric currents.		Ratio $\frac{S}{N}$.
	Selective effect (S).	Normal effect (N).	
404 volts.	$1 \cdot 00$ ($= 295 \times 10^{-12}$ amp.)	$1 \cdot 00$ ($= 11 \cdot 4 \times 10^{-12}$ amp.)	$1 \cdot 00$
302	$\cdot 962$	$\cdot 910$	$1 \cdot 06$
129	$\cdot 723$	$\cdot 628$	$1 \cdot 15$
87	$\cdot 627$	$\cdot 528$	$1 \cdot 19$
44	$\cdot 463$	$\cdot 320$	$1 \cdot 26$
18	$\cdot 307$	$\cdot 212$	$1 \cdot 45$
12·8	$\cdot 261$	$\cdot 173$	$1 \cdot 51$
8·0	$\cdot 209$	$\cdot 133$	$1 \cdot 57$
3·9	$\cdot 115$	$\cdot 0712$	$1 \cdot 61$
2·00	$\cdot 0522$	$\cdot 0291$	$1 \cdot 79$
1·46	$\cdot 0308$	$\cdot 0160$	$1 \cdot 93$
1·00	$\cdot 0116$	$\cdot 0055$	$2 \cdot 07$

were carried out with the same aperture at the lens for both planes of polarization. In these cases, the selective effect with 404 volts accelerating potential was 25·9 times larger than the normal effect. In other cases, the lens was stopped down to one twenty-sixth part of its area when the selective effect was being measured, so as to make the selective and normal effects of the same order of magnitude. The

results obtained were consistent, as was to be expected. It is clear that the ratio of the selective effect to the normal increases slowly as the accelerating potential decreases. In other words, the electrons in the selective effect tend to follow the electric field somewhat more readily than those in the normal effect. The results are plotted in fig. 4. The

Fig. 4.

curve for the selective effect has practically become flat with 404 volts, showing that all the electrons emitted from the alloy, whatever be their direction of emission, have been received by the electrode E. It is unfortunate that accelerating potentials greater than 404 volts could not be used in order to find where the normal curve became flat. We may, however, estimate that the normal curve becomes flat at about 500 volts. It is worthy of note that by multiplying the coordinates of the normal curve by suitable factors, the normal curve can be brought into close coincidence with the selective curve.

These experiments show that there is a small difference in the way in which the electrons are emitted in the two effects, although it is quite small in comparison with the difference in the order of magnitude of the two effects. Is this difference due to a difference in the *velocity* with which the electrons are emitted, or to a difference in the *direction* in

which they are emitted? If the selective electrons were slower than the normal electrons, but had identical direction distributions, then the smaller potentials would suffice to gather the same fraction of the total number of electrons emitted from the alloy into the electrode E. On the other hand, if the velocity distributions in both effects were the same, but if the concentration of electrons along directions near the normal were greater in the selective effect than in the normal effect, then again it would require smaller potentials to gather in a given fraction of the selective electrons than of the normal electrons. Hence we cannot decide from these experiments whether the curves imply a difference between the velocity distributions in the two cases, or in the direction distributions. To find out exactly the origin of the difference between the curves in fig. 4 would require a more elaborate experiment. It will probably be necessary to investigate both the direction distributions of the electrons and also their velocity distributions along each direction. The maximum emission velocity could be measured by noting the least potential applied to the alloy which would keep the electrode E from receiving any electrons. Owing to the arrangement of the electrode E relative to the illuminated alloy, the apparatus was very insensitive for the test. A difference in the maximum energies of ·15 volt could have been detected ; no difference could be observed in these experiments. Richardson and Compton, Kadesch, and Millikan, using unpolarized light, found that the maximum emission energy of the photo-electrons was a linear function of the frequency. Thus there is no indirect evidence from these results of any departure in the selective effect from the law obeyed by the normal effect.

Experiments such as those made by Pohl and Pringsheim on the numbers of electrons liberated from the alkali metals by polarized light point to a fundamental difference between the two effects. The appearance of the curve for the selective effect suggests strongly that we have to deal with some kind of a resonance effect, and that each alkali metal contains electronic systems whose frequency is characteristic of the metal. These systems become unstable the more readily, the closer the frequency of the incident light to this characteristic frequency. The electrons associated with the normal effect are not related to any system possessing a frequency characteristic of the metal. Thus, investigations of the number of electrons emitted in the selective and in the normal effects suggest different origins for the two effects. But there is no evidence from the various experiments on the

velocities of the electrons for the view that the two effects are fundamentally different. If then, for a moment, we assume that the two effects are ultimately identical, we must look for some intermediate effect which can account for the great difference in the number of electrons emitted. If, over a certain range of wave-lengths, the light polarized in the E$_{\parallel}$ plane were absorbed with unusual rapidity in the surface layers, then we should expect an unusually large emission of electrons, for they would have a greater opportunity of emerging than if they had been released in the deeper layers. The optical properties of the alkali metals in the region of the selective effect are unknown, and therefore there is no evidence to justify this conjecture. We cannot say that, in the case of those metals whose optical properties have been investigated in some detail, there is any evidence to support such a view as advanced above, but then these metals exhibit only the normal photo-electric effect.

Summary.

Although the number of the photo-electrons emitted in the selective photo-electric effect of the sodium-potassium alloy used in these experiments is twenty-six times as great as the number emitted in the normal photo-electric effect, yet the way in which the two sets of electrons are emitted differs only to a small extent. This small difference may arise either from a somewhat smaller average velocity of the photo-electrons emitted in the selective effect, or else from a greater proportion of the selective photo-electrons being emitted in directions closer to the normal to the surface. These results on the velocities of the photo-electrons in the selective and normal effects are hardly to be expected, if one concludes that the great difference in the magnitude of the two effects, and also their relation to the frequency of the light used, indicates a fundamental difference between the two effects.

XV. *Note on the Partial Fraction Problem.*
By I. J. Schwatt [*].

TO the methods I have given before † I add the following :
I. To separate

$$F(x) = \frac{\sum\limits_{a=0}^{n} m_a x^{n-a}}{\prod\limits_{\beta=1}^{p} (x^2 + c_\beta^2)}, \text{ where } n < 2p,$$

into partial fractions.

$$F(x) = \sum_{\beta=1}^{p} \frac{A_\beta x + B_\beta}{x^2 + c_\beta^2} \quad . \quad . \quad . \quad . \quad (1)$$

This relation may be written

$$F(x) = \frac{A_\kappa x + B_\kappa}{x^2 + c_\kappa^2} + \frac{\psi_\kappa(x)}{\phi_\kappa(x)}, \quad . \quad . \quad . \quad (2)$$

where

$$\phi_\kappa(x) = \prod_{\gamma=1}^{\kappa-1} (x^2 + c_\gamma^2) \prod_{\gamma=\kappa+1}^{p} (x^2 + c_\gamma^2).$$

From (2) follows

$$\sum_{a=0}^{n} m_a x^{n-a} = (A_\kappa x + B_\kappa)\phi_\kappa(x) + (x^2 + c_\kappa^2)\psi_\kappa(x). \quad . \quad (3)$$

Substituting in this identity ic_κ for x, we have

$$\sum_{a=0}^{n} m_a c_\kappa^{n-a} i^{n-a} = \phi_\kappa(ic_\kappa)(A_\kappa ic_\kappa + B_\kappa) \quad . \quad . \quad (4)$$

To obtain A_κ and B_κ we separate the first member of (4)
into its real and imaginary parts.

We have

$$\sum_{a=0}^{n} m_a c_\kappa^{n-a} i^{n-a} = \sum_{a=0}^{n} m_{n-a} c_\kappa^a i^a = m_n - m_{n-2} c_\kappa^2 + m_{n-4} c_\kappa^4 - \dots.$$

$$+ (-1)^{\left[\frac{n}{2}\right]} m_{n-2\left[\frac{n}{2}\right]} c_\kappa^{2\left[\frac{n}{2}\right]} + i \left[m_{n-1} c_\kappa - m_{n-3} c_\kappa^3 \right.$$

$$\left. + m_{n-5} c_\kappa^5 - \dots. + (-1)^{\left[\frac{n-1}{2}\right]} m_{n-2\left[\frac{n-1}{2}\right]-1} c_\kappa^{2\left[\frac{n-1}{2}\right]+1} \right],$$

or

$$\sum_{a=0}^{n} m_a c_\kappa^{n-a} i^{n-a} = \sum_{a=0}^{\left[\frac{n}{2}\right]} (-1)^a m_{n-2a} c_\kappa^{2a} + i \sum_{a=0}^{\left[\frac{n-1}{2}\right]} (-1)^a m_{n-2a-1} c_\kappa^{2a+1}. \quad (5)$$

Therefore

$$A_\kappa c_\kappa \phi(ic_\kappa) = \sum_{a=0}^{\left[\frac{n-1}{2}\right]} (-1)^a m_{n\ 2a-1} c_\kappa^{2a+1}$$

or

$$A_\kappa = \frac{\displaystyle\sum_{a=0}^{\left[\frac{n-1}{2}\right]} (-1)^a m_{n-2a-1} c_\kappa^{2a}}{\displaystyle\prod_{\gamma=1}^{\kappa-1} (c_\gamma^2 - c_\kappa^2) \prod_{\gamma=\kappa+1}^{p} (c_\gamma^2 - c_\kappa^2)} \quad . \quad . \quad . \quad (6)$$

and

$$B_\kappa = \frac{\displaystyle\sum_{a=0}^{\left[\frac{n}{2}\right]} (-1)^a m_{n-2a} c_\kappa^{2a}}{\displaystyle\prod_{\gamma=1}^{\kappa-1} (c_\gamma^2 - c_\kappa^2) \prod_{\gamma=\kappa+1}^{p} (c_\gamma^2 - c_\kappa^2)} \quad . \quad . \quad . \quad (7)$$

Hence

$$\frac{\displaystyle\sum_{a=0}^{n} m_a x^{n-a}}{\displaystyle\prod_{\beta=1}^{p} (x^2 + c_\beta^2)} \sum_{\kappa=1}^{p} \cdot \frac{\left(\displaystyle\sum_{a=0}^{\left[\frac{n-1}{2}\right]} (-1)^a m_{n-2a-1} c_\kappa^{2a}\right) x + \displaystyle\sum_{a=0}^{\left[\frac{n}{2}\right]} (-1)^a m_{n-2a} c_\kappa^{2a}}{x^2 + c_\kappa^2}.$$

II. To separate

$$F(x) = \frac{\displaystyle\sum_{a=0}^{n} m_a x^{n-a}}{(x^2 + c^2)^p}, \text{ where } n < 2p,$$

into Partial Fractions,

$$\frac{\displaystyle\sum_{a=0}^{n} m_a x^{n-a}}{(x^2 + c^2)^p} = \sum_{\kappa=0}^{p-1} \frac{A_\kappa x + B_\kappa}{(x^2 + c^2)^{p-\kappa}}, \quad . \quad . \quad . \quad (1)$$

or

$$\sum_{a=0}^{n} m_a x^{n-a} = \sum_{\kappa=0}^{p-1} (A_\kappa x + B_\kappa)(x^2 + c^2)^\kappa \quad . \quad . \quad . \quad (2)$$

Equating the odd powers of both sides of this identity, and also the even powers, we obtain

$$\sum_{a=0}^{\left[\frac{n-1}{2}\right]} m_{n-2a-1} x^{2a} = \sum_{\kappa=0}^{p-1} A_\kappa (x^2 + c^2)^\kappa, \quad . \quad . \quad . \quad (3)$$

and

$$\sum_{a=0}^{\left[\frac{n}{2}\right]} m_{n-2a} x^{2a} = \sum_{\kappa=0}^{p-1} B_\kappa (x^2 + c^2)^\kappa. \quad . \quad . \quad . \quad (4)$$

Differentiating (3) and (4) h times with respect to x^2, and letting $x^2 = -c^2$, we have

$$A_h = \sum_{a=h}^{\left[\frac{n-1}{2}\right]} (-1)^{a-h} m_{n-2a-1} c^{2(a-h)} \binom{\alpha}{h},$$

and

$$B_\kappa = \sum_{a=h}^{\left[\frac{n}{2}\right]} (-1)^{a-h} m_{n-2a} c^{2(a-h)} \binom{\alpha}{h}.$$

Therefore

$$\frac{\sum\limits_{a=0}^{n} m_a x^{n-a}}{(x^2+c^2)^p} = \sum_{\kappa=0}^{p-1} \left[\left(\sum_{\alpha=\kappa}^{\left[\frac{n-1}{2}\right]} (-1)^{a-\kappa} \binom{\alpha}{\kappa} m_{n-2a-1} c^{2(\alpha-\kappa)} \right) x \right.$$
$$\left. + \sum_{\alpha=\kappa}^{\left[\frac{n}{2}\right]} (-1)^{a-\kappa} \binom{\alpha}{\kappa} m_{n-2a} c^{2(\alpha-\kappa)} \right] \frac{1}{(x^2+c^2)^{p-\kappa}}.$$

III. To separate

$$S = \frac{\prod\limits_{\kappa=1}^{p} (x+a_\kappa)}{\prod\limits_{\kappa=1}^{q} (x^2+b_\kappa)}, \text{ where } p < 2q,$$

into partial fractions.

Now

$$\prod_{\kappa=1}^{p} (a_\kappa + x) = \frac{\prod\limits_{\kappa=1}^{p} (a_\kappa + x) + \prod\limits_{\kappa=1}^{p} (a_\kappa - x)}{2} + \frac{\prod\limits_{\kappa=1}^{p} (a_\kappa + x) - \prod\limits_{\kappa=1}^{p} (a_\kappa - x)}{2},$$

the first part being of even and the second of odd degree.

Hence we may denote

$$\frac{\prod\limits_{\kappa=1}^{p} (a_\kappa + x) + \prod\limits_{\kappa=1}^{p} (a_\kappa - x)}{2} = \phi(x^2),$$

and

$$\frac{\prod\limits_{\kappa=1}^{p} (a_\kappa + x) - \prod\limits_{\kappa=1}^{p} (a_\kappa - x)}{2} = x\Theta(x^2).$$

Therefore

$$S = x \frac{\Theta(x^2)}{\prod\limits_{\kappa=1}^{q} (x^2+b_\kappa)} + \frac{\phi(x^2)}{\prod\limits_{\kappa=1}^{q} (x^2+b_\kappa)}.$$

Now

$$\frac{\Theta(x^2)}{\prod\limits_{\kappa=1}^{q}(x^2+b_\kappa)} = \sum_{n=1}^{q}\frac{A_n}{x^2+b_n},$$

therefore

$$A_n = \frac{\Theta(-b_n)}{\prod\limits_{\kappa=1}^{n-1}(b_\kappa-b_n)\prod\limits_{\kappa=n+1}^{q}(b_\kappa-b_n)}.$$

Similarly

$$\frac{\phi(x^2)}{\prod\limits_{\kappa=1}^{q}(x^2+b_\kappa)} = \sum_{n=1}^{q}\frac{B_n}{x^2+b_n},$$

and

$$B_n = \frac{\phi(-b_n)}{\prod\limits_{\kappa=1}^{n-1}(b_\kappa-b_n)\prod\limits_{\kappa=n+1}^{q}(b_\kappa-b_n)},$$

and therefore

$$S = \sum_{n=1}^{q}\frac{x\Theta(-b_n)+\phi(-b_n)}{\prod\limits_{\kappa=1}^{n-1}(b_\kappa-b_n)\prod\limits_{\kappa=n+1}^{q}(b_\kappa-b_n)}\cdot\frac{1}{x^2+b_n}.$$

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XVI. *The Sum of a Series of Cosecants.* By G. N. WATSON, *M.A., Fellow of Trinity College, Cambridge, Assistant Professor of Pure Mathematics at University College, London* [*].

1. IN modern theories of the structure of the atom, the usual assumption is that it consists of a ring of electrons (repelling one another according to the ordinary inverse square law) rotating, in the normal configuration of the atom, in a symmetrical manner round a small positive charge.

If n be the number of electrons, each of charge $-e$ and mass m, and the positive charge be of magnitude νe (where ν may or may not be equal to n), while the radius of the atom is a, it is easily shown that, in steady circular motion, the angular velocity ω of the system is given by the formula

$$\omega^2 = \frac{e^2}{ma^3}(\nu-\tfrac{1}{4}S_n),$$

where

$$S_n = \operatorname{cosec}\frac{\pi}{n} + \operatorname{cosec}\frac{2\pi}{n} + \ldots + \operatorname{cosec}\frac{(n-1)\pi}{n}$$

$$= \sum_{m=1}^{n-1}\operatorname{cosec}(m\pi/n).$$

The expression $\nu - \frac{1}{4}S_n$ plays a very important part in the investigation of oscillations about the steady motion, as well as in Bohr's theory of spectra; and an analogous expression obviously occurs in the gravitational problem of a number of equal satellites rotating in a circle about a planet—a simplified form of the problem of Saturn's rings, considered by Clerk-Maxwell.

Reference may also be made to Sir **J. J. Thomson**, Phil. Mag. (6) vii. (1904) p. 237, to G. A. Schott, 'Electromagnetic Radiation,' and to various recent papers by **J. W. Nicholson** * in the Monthly Notices of the R.A.S.

For large values of n, the labour of numerical calculation, in determining S_n directly, is obviously severe; to avoid this labour the need arises for a suitable asymptotic formula for the sum

$$S_n = \sum_{m=1}^{n-1} \operatorname{cosec}(m/\pi n) ;$$

in this paper a complete asymptotic expansion of S_n is obtained, and, by means of this expansion, S_n is tabulated for various values of n from 6 to 100 and also for $n = 360$, $n = 1000$.

2. By using Euler's well-known formula

$$\int_0^\infty \frac{x^{a-1}dx}{1+x} = \frac{\pi}{\sin a\pi}, \quad (0 < a < 1)$$

we see at once that

$$\begin{aligned}
\pi S_n &= \int_0^\infty \frac{1}{x(1+x)} \{x^{1/n} + x^{2/n} + \ldots + x^{(n-1)/n}\} dx \\
&= \int_0^\infty \frac{(x^{1/n} - x)dx}{x(1+x)(1-x^{1/n})} \\
&= n\int_0^\infty \frac{(1-y^{n-1})dy}{(1+y^n)(1-y)} \\
&= n\int_{-\infty}^\infty \frac{(1-e^{-(n-1)t})dt}{(1+e^{-nt})(e^t-1)} \\
&= 2n\int_0^\infty \frac{(1-e^{-(n-1)t})dt}{(1+e^{-nt})(e^t-1)},
\end{aligned}$$

on summing the geometrical progression and then writing $x^{1/n} = y = e^{-t}$; the final step, of bisecting the range of integration, is justified by the fact (which is readily verified) that the integrand is an *even* function of t.

* To whom I am indebted for pointing out the desirability of discovering the results contained in this paper.

3. The first stage of the analysis is now complete: it remains to transform the integral, which has just been obtained, into a form suitable for calculation when n is large. The following method is the only one, of several which I investigated, which produces the desired result:

First transform the integrand thus,

$$\frac{1-e^{-(n-1)t}}{(1+e^{-nt})(e^t-1)} = \frac{1}{e^t-1} - \frac{2e^{-nt}}{1+e^{-nt}}\left\{\frac{1}{et-1} + \frac{1}{2}\right\}$$

$$= \left[\frac{1}{e^t-1} - \frac{e^{-t}}{t}\right] + \left[\frac{e^{-t}}{t} - \frac{2e^{-nt}}{1+e^{-nt}}\left\{\frac{1}{e^t-1} + \frac{1}{2}\right\}\right];$$

the terms e^{-t}/t are inserted to secure the convergence of the integrals of the expressions contained in square brackets. It is well known that

$$\int_0^\infty \left\{\frac{1}{e^t-1} - \frac{e^{-t}}{t}\right\} dt = \gamma,$$

where γ is Euler's constant (see, *e. g.*, Whittaker and Watson, 'Modern Analysis,' p. 240).

Now [*]

$$\frac{1}{e^t-1} = \frac{1}{t} - \frac{1}{2} + B_1\frac{t}{2!} - B_2\frac{t^3}{4!} + \ldots + (-)^{r-1}B_r\frac{t^{2r-1}}{(2r)!}$$
$$+ (-)^r\theta B_{r+1}\frac{t^{2r+1}}{(2r+2)!},$$

where $0 \leq \theta \leq 1$ when $t \geq 0$, r is any positive integer, and $B_1, B_2, \ldots$ are Bernoulli's numbers.

On substitution in the second part of the integrand connected with πS_n, we get

$$\pi S_n = 2n\gamma + 2n\int_0^\infty \left\{\frac{e^{-t}}{t} - \frac{2e^{-nt}}{(1+e^{-nt})t}\right\} dt$$

$$+ 2n\int_0^\infty \frac{2e^{-nt}}{1+e^{-nt}}\left\{\sum_{m=1}^r (-)^m B_m\frac{t^{2m-1}}{(2m)!} + (-)^{r+1}\theta B_{r+1}\frac{t^{2r+1}}{(2r+2)!}\right\} dt$$

$$= 2n\int_0^\infty \frac{e^{-t}-e^{-nt}}{t} dt + 2n\int_0^\infty \left\{e^{-nt} - \frac{2e^{-nt}}{1+e^{-nt}}\right\}\frac{dt}{t} + 2n\gamma$$

$$+ 4n\sum_{m=1}^r \frac{(-)^m B_m}{(2m)!} I_{2m-1} + 4n\frac{\theta_1(-)^{r+1}B_{r+1}}{(2r+2)!} I_{2r+1}$$

where

$$I_m = \int_0^\infty \frac{e^{-nt}t^m dt}{1+e^{-nt}} = \frac{1}{n^{m+1}}\int_0^\infty \frac{u^m du}{e^u+1};$$

and $0 \leq \theta_1 \leq 1$, by the first mean-value theorem, because $0 \leq \theta \leq 1$ and the integrand involved in I_{2r+1} is *positive*.

[*] Bromwich, 'Infinite Series,' p. 234.

If we use Frullani's formula

$$\int_0^\infty (e^{-t} - e^{-nt})t^{-1}dt = \log n,$$

and write $nt = u$, the formula for πS_n becomes

$$\pi S_n = 2n \log n + 2n \left\{ \gamma - \int_0^\infty \frac{1 - e^{-u}}{e^u + 1} \frac{du}{u} \right\}$$

$$+ 4 \sum_{m=1}^r \frac{(-)^m B_m}{(2m)! \, n^{2m-1}} \int_0^\infty \frac{u^{2m-1}du}{e^u + 1} + 4\theta_1 \frac{(-)^{r+1}B_{r+1}}{(2r+2)! \, n^{2r+1}} \int_0^\infty \frac{u^{2r+1}du}{e^u + 1}.$$

It will be observed that n no longer appears under the integral signs, so that this result may be expected to give the required asymptotic expansion when the integrals have been evaluated.

To evaluate the integrals, let $\alpha > -1$; then

$$\int_0^\infty \frac{u^m \, du}{e^u + 1} = (-)^m \int_0^\infty \left[\frac{\partial^m}{\partial \alpha^m} \frac{e^{-\alpha u}}{e^u + 1} \right]_{\alpha=0} du$$

$$= (-)^m \left[\frac{\partial^m}{\partial \alpha^m} \int_0^\infty \frac{e^{-\alpha u}du}{e^u + 1} \right]_{\alpha=0},$$

the change of order of differentiation and integration being easily justified since $\alpha > -1$ (Bromwich, 'Infinite Series,' pp. 436, 437).

Now, α being greater than -1, we have

$$\int_0^\infty e^{-\alpha u}(e^u + 1)^{-1}du = \int_0^\infty e^{-\alpha u} \left\{ e^{-u} - e^{-2u} + \ldots + (-)^{p-1}e^{-pu} \right.$$

$$\left. + (-)^p \frac{e^{-pu}}{e^u + 1} \right\} du$$

$$= \frac{1}{\alpha + 1} - \frac{1}{\alpha + 2} + \ldots + \frac{(-)^{p-1}}{\alpha + p}$$

$$+ (-)^p \int_0^\infty \frac{e^{-(\alpha+p)u}du}{e^u + 1}.$$

Now

$$0 < \int_0^\infty \frac{e^{-(\alpha+p)u}du}{e^u + 1} < \int_0^\infty e^{-(\alpha+p+1)u}du$$

$$= 1/(\alpha + p + 1),$$

and this tends to zero as p tends to infinity.

Thus we have

$$\int_0^\infty \frac{e^{-au}du}{e^u+1} = \frac{1}{\alpha+1} - \frac{1}{\alpha+2} + \frac{1}{\alpha+3} - \cdot \cdot \cdot$$

$$= \tfrac{1}{2}\{\psi(\tfrac{1}{2}\alpha+1) - \psi(\tfrac{1}{2}\alpha+\tfrac{1}{2})\},$$

where ψ is the logarithmic derivate of the Gamma-function. It follows at once that

$$\int_0^\infty \frac{u^m du}{e^u+1} = (-)^m 2^{-m-1}\{\psi^{(m)}(1) - \psi^{(m)}(\tfrac{1}{2})\}.$$

Now, when $m \geq 1$,

$$\psi^{(m)}(1) = (-)^{m-1}m!\left\{\frac{1}{1^{m+1}} + \frac{1}{2^{m+1}} + \ldots\right\}$$

$$= (-)^{m-1}m!\,\sigma_{m+1}, \quad \text{say ;}$$

and

$$\psi^{(m)}(\tfrac{1}{2}) = (-)^{m-1}m!\left\{\frac{1}{(\tfrac{1}{2})^{m+1}} + \frac{1}{(\tfrac{3}{2})^{m+1}} + \ldots\right\}$$

$$= (-)^{m-1}2^{m+1}m!\left\{\sigma_{m+1} - \frac{1}{2^{m+1}} - \frac{1}{4^{m+1}} - \ldots\right\}$$

$$= (-)^{m-1}(2^{m+1}-1)\,.\,m!\,\sigma_{m+1}.$$

Consequently

$$\int_0^\infty \frac{u^m du}{e^u+1} = m!\,(1-2^{-m})\sigma_{m+1}.$$

Finally, we have to evaluate

$$\int_0^\infty \frac{1-e^{-u}}{e^u+1}\,\frac{du}{u} = \int_0^\infty \frac{1}{e^u+1}\left\{\int_0^1 e^{-au}d\alpha\right\}du$$

$$= \int_0^1 \left\{\int_0^\infty \frac{e^{-au}du}{e^u+1}\right\}d\alpha$$

$$= \int_0^1 \left\{\tfrac{1}{2}\psi(\tfrac{1}{2}\alpha+1) - \psi(\tfrac{1}{2}\alpha+\tfrac{1}{2})\right\}d\alpha$$

$$= \log\frac{\Gamma(\tfrac{3}{2})}{\Gamma(1)} - \log\frac{\Gamma(1)}{\Gamma(\tfrac{1}{2})}$$

$$= \log\pi - \log 2\,;$$

the change of order of integration being justified, since $\alpha > -1$ on the range of integration.

On collecting our results, we now see that

$$\pi S_n = 2n \log_e (2n) + 2n\{\gamma - \log \pi\}.$$

$$+ 2 \sum_{m=1}^{r} \frac{(-)^m B_m (1 - 2^{1-2m}) \sigma_{2m}}{m \cdot n^{2m-1}} + 2\theta_1 \frac{(-)^{r+1} B_{r+1} (1 - 2^{-1-2r}) \sigma_{2r+2}}{(r+1) \cdot n^{2r+1}}$$

This formula obviously has the property (which is *sufficient* to give an asymptotic expansion) that the remainder after r terms of the series on the right has the same sign and is numerically less than the $(r+1)$th term, and this $(r+1)$th term tends to zero as n tends to infinity, r remaining fixed.

By using the known formula $\sigma_{2m} = 2^{2m-1} \pi^{2m} B_m / (2m)!$ we may, if we wish, write

$$\frac{(-)^m B_m^2 \pi^{2m} (2^{2m} - 2)}{m \cdot (2m)!} \quad \text{for} \quad \frac{(-)^m 2 B_m (1 - 2^{1-2m}) \sigma_{2m}}{m}$$

in the series on the right.

4. For purposes of tabulation we make use of the values given for σ_{2m} in Chrystal's 'Algebra,' ii. p. 367.

The first few terms of the expansion then give the approximate result

$$S_n = 2n[0{\cdot}7329355992 \times \log_{10}(2n) - 0{\cdot}1806453871] - n^{-1} \times 0{\cdot}087266$$
$$+ n^{-3} \times 0{\cdot}01035 - n^{-5} \times 0{\cdot}004 + n^{-7} \times 0{\cdot}005.$$

In the construction of the following table the term in n^{-5} could be neglected throughout, and the term in n^{-3} could be neglected when $n > 20$.

It is worth observing that, in the special case in which the charge of the nucleus is numerically equal to the total charge of the electrons composing the ring, the expression for ω^2 given in § 1 yields a real value for ω only when $n - \frac{1}{4} S_n > 0$, i. e. when $n \leq 472$.

5. The analogous series

$$T_n = \sum_{m=1}^{n-1} \operatorname{cosec} \left(\frac{m\pi}{n} - \frac{1}{2}\beta \right)$$

may be investigated in a manner similar to that in which S_n was considered. This series occurs in the radial component of force on an electron rotating round a nucleus in company with $n-1$ other electrons, when that particular electron is displaced along the circle an angular distance β from its position in steady motion; it is supposed that $-2\pi/n < \beta < 2\pi/n$.

n.	S_n.	n.	S_n.
2*	1·00000	25	53·22602
3*	2·30940	26	56·00452
4*	3·82843	27	58·80752
5*	5·50552	28	61·63406
6	7·30938	29	64·48341
7	9·21906	30	67·35460
8	11·21946	35	82·01599
9	13·29332	40	97·13358
10	15·44980	45	112·65005
11	17·66388	50	128·52084
12	19·93579	55	144·71045
13	22·26070	60	161·18983
14	24·63456	65	177·93472
15	27·05387	70	194·92471
16	29·51559	75	212·14226
17	32·01709	80	229·57213
18	34·55603	85	247·20108
19	37·13041	90	265·01741
20	39·74028	95	283·01061
21	42·37770	100	301·17141
22	45·04863	360	1377·78855
23	47·74646	1000	4477·59415
24	50·47299		

* The values of S_n for $n=2, 3, 4, 5$ were calculated directly and not from the asymptotic expansion.

By the methods employed in §§ 2, 3 we get

$$\pi T_n = 2n \int_0^\infty \cosh\left(\frac{n\beta t}{2\pi}\right) \cdot \frac{(1-e^{-(n-1)t})\,dt}{(1+e^{-nt})(e^t-1)}$$

$$= 2n \int_0^\infty \cosh(\lambda nt) \cdot \frac{(1-e^{-(n-1)t})\,dt}{(1+e^{-nt})(e^t-1)},$$

where $\lambda = \beta/(2\pi)$; it then follows that

$$\pi T_n = 2n \int_0^\infty \left\{ \frac{\cosh(\lambda nt)}{e^t-1} - \frac{e^{-t}}{t} \right\} dt + 2n \int_0^\infty \frac{e^{-t}-e^{-nt}}{t}\,dt$$

$$+ 2n \int_0^\infty \left\{ \frac{e^{-nt}}{t} - \frac{2e^{-nt}\cosh(\lambda nt)}{(1+e^{-nt})t} \right\} dt$$

$$+ 4 \sum_{m=1}^r \frac{(-)^m B_m}{(2m)!\,n^{2m-1}} J_{2m-1} + 4\theta_2 \frac{(-)^{r+1} B_{r+1}}{(2r+2)!\,n^{2r+1}} J_{2r+1},$$

where

$$J_m = \int_0^\infty \frac{u^m \cosh \lambda u}{e^u+1}\,du,$$

and

$$0 \leq \theta_2 \leq 1.$$

On using the formula of Gauss

$$\psi(z) = \int_0^\infty \left\{ \frac{e^{-t}}{t} - \frac{e^{-zt}}{1 - e^{-t}} \right\} dt,$$

we get, without much difficulty,

$$\pi T_n = 2n \left[\log \left\{ \lambda n \cot \left(\tfrac{1}{2} \lambda \pi \right) \right\} - \tfrac{1}{2} \psi (1 - \lambda n) - \tfrac{1}{2} \psi (1 + \lambda n) \right]$$
$$+ \sum_{m=1}^{n-1} \frac{(-)^m B_m}{(2m)!\,(2n)^{2m-1}} \left\{ \psi^{(2m-1)} \left(\tfrac{1}{2} - \tfrac{1}{2} \lambda \right) + \psi^{(2m-1)} \left(\tfrac{1}{2} + \tfrac{1}{2} \lambda \right) \right.$$
$$\left. - \psi^{(2m-1)} \left(1 - \tfrac{1}{2} \lambda \right) - \psi^{(2m-1)} \left(1 + \tfrac{1}{2} \lambda \right) \right\},$$

the remainder after r terms having the same sign and being numerically less than the $(r+1)$th term; where λ is equal to $\beta/(2\pi)$.

The corresponding series occurring in the transverse component of force is

$$U_n = \sum_{m=1}^{n-1} \cos \left(\frac{m\pi}{n} - \frac{1}{2} \beta \right) \operatorname{cosec}^2 \left(\frac{m\pi}{n} - \frac{1}{2} \beta \right)$$
$$= 2 \frac{\partial T_n}{\partial \beta} = \frac{1}{\pi} \frac{\partial T_n}{\partial \lambda};$$

this may be determined from the asymptotic expansion for T_n, which may legitimately be differentiated term by term with respect to λ.

XVII. *On the Cooling of Cylinders in a Stream of Air. By* Pte. J. ALFRED HUGHES, *B.Sc., E Coy, R.A.M.C., formerly Research Student, University College of North Wales, Bangor*[*].

THE interchange of heat between a solid and a moving stream of gas is a subject of considerable technical importance, and also not devoid of scientific interest. A considerable amount of work has been done on the cooling of thin wires[†] in a current of air, mainly with the object of constructing instruments for the measurements of air-velocity. These experiments have shown that the heat lost by the wire is proportional to the difference of temperature and to the square-root of the velocity. There are, however, no data available relating to the convection of heat from bodies of large diameters; and the following experiments were undertaken with a view of throwing some light on the problem of convection in these cases.

Apparatus.

The measurements were carried out on a series of copper tubes all of the same length, but with external diameters ranging from ·433 cm. to 5·06 cm.   These tubes, of about a metre in length, were placed vertically in the wind-channel, and were heated by steam from a boiler placed on top of the channel; after a steady temperature was attained, the weight of the water which condensed in the cylinder in a given time measured the heat which it lost through convection and radiation.

The wind-channel, fig. 2, consisted of a wooden tunnel placed horizontally, which was of square section, of side 3 feet, and was 10 feet long.   This terminated in a rectangular box of greater section in which the fan rotated.
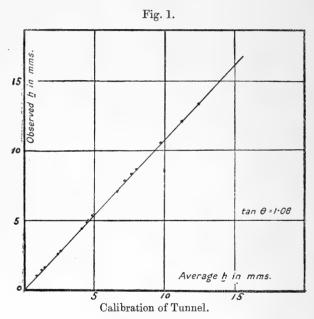
The fan was made by attaching four narrow steel blades to the axle of a three-phase motor, the speed of which could be regulated (*a*) by a rotor rheostat, and (*b*) by varying the voltage of the alternator supplying the current.   A good range of wind-velocity could thus be obtained.   The velocity of the air currents produced by the fan was measured by the ordinary Pitot-tube and gauge.   This consisted of two glass tubes of $\frac{3}{16}$ inch bore, the dynamic tube facing the wind, and the static tube being placed with the plane of its orifice parallel to the direction of the flow.   These tubes were placed close to one another in the centre of the channel, immediately in front of the cooling cylinder.   By means of rubber tubing they were connected to a water-gauge, the difference of level in which measured the difference of pressure, which was proportional to the square of the velocity as given by

$$v = \sqrt{2gh},$$
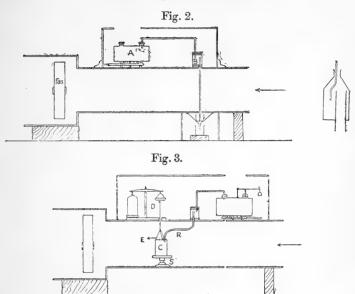
h being the pressure difference in metres of air, and v the velocity in metres per second.   The difference between the two sides of the U-tube was measured by a cathetometer microscope reading to $\frac{1}{100}$ of a millim.   The gauge-tubes were 2 cm. wide so as to avoid surface-tension errors.   Large oscillations were produced in the liquid in the gauge on account of variation in the wind-pressure, and this caused a difficulty in measuring the wind-velocity.   The oscillations were damped, and the amplitude reduced by loosely stopping the bottom of the U-tube with cotton-wool.   In some of the later experiments, thick paraffin was adopted as the liquid in the gauge.   With this, the difference of level was increased on account of the smaller density of the liquid, while the oscillations were reduced by reason of its greater viscosity.

The Pitot-tube determined the wind-velocity at the middle of the channel; and since an average value of the velocity over the cylinder was required, a determination was made of how the wind-velocity varied along a vertical line through the position of the Pitot-tube. A reading was taken with the Pitot-tube in its ordinary position : then readings were taken for the same wind velocity at different points across the channel. Thus an average value was calculated for the channel, and this was done for different velocities of the wind. A graph was plotted (fig. 1) showing the relation between the Pitot-tube reading at the centre of the channel and the average reading for the section. From this an average value can be read for any value of the axial wind-velocity.

Fig. 1.

Calibration of Tunnel.

The heat lost was determined by finding the weight of water condensed. The arrangement of the steam generator is shown in fig. 2. The boiler A is placed on the top of the channel, and the steam passes into the top of the tube through the water-trap B placed directly over the tube. The whole was shielded from air-currents by an asbestos cover. With cylinders of the largest diameters and with the stream-line tubes, a metallic steam-trap covered with cotton-wool was used, and the tubes were soldered to the bottom of the can as shown in the diagram.

The condensed water was collected in a beaker placed underneath the tubes, a glass funnel being attached to the bottom end of the copper tube to ensure that all the condensed water should be caught in the beaker ; the excess of

Fig. 2.

Fig. 3.

steam which came out with the condensed water escaped to the air past the sides of the tube. The end of the copper tube and the funnel were covered with cotton-wool. A wooden box was built round this receiving apparatus beneath the wind-channel, to shield it from air currents produced by the fan.

The experiment was carried on in the following manner. The water was boiled and the steam allowed to pass through the copper tube for about five minutes, to ensure that the steady temperature had been attained.

The first reading of the Pitot-tube was taken, the motor started, and after a short interval, a weighed beaker was placed underneath the end of the cylindrical tube, and the stop-watch started. Readings of the water "head" in the Pitot-tube gauge were registered, and after 10 minutes the beaker was taken away, and the motor stopped. The second zero of the gauge was taken, and the beaker and water weighed. The temperature of the air and the atmospheric pressure were also taken.

In the case of the large cylinder, 20 cm. length, 15·5 cm. diameter, the arrangement of the apparatus is shown in fig. 3. The condensed water was allowed to collect in the cylinder C itself, the whole being suspended from a balance B placed on the top of the channel, the steam connexion being made by rubber-tubing R. When the balance-beam is down, the cylinder rests on a stand S in the channel ; the excess of steam escapes through the exit E.

The water condensed, which measures the heat lost, is estimated by taking the weight of the cylinder at the beginning and end of the interval of time, viz. 10 minutes. Steam is passed through for about 5 minutes, and after the steady temperature has been attained, the weight is taken and the motor started. After 10 minutes the motor is stopped and the weight again taken. The weight of the water condensed will be the sum of three parts : (1) that condensed by convection and radiation in still air in the interval from the first weighing till the motor was started; (2) the condensation during the wind-current; (3) the condensation in still air during the interval between the stopping of the motor and the time when the final weight is taken. The "water equivalent" of the excess of time above 10 minutes is found, and this subtracted from the total weight gives the weight of water condensed by the wind alone. Still-air condensation is small, as can be seen from Table II., and therefore no serious error is introduced by this method.

Corrections.

Most of the heat is lost from the cooling cylinders by convection, but some also by radiation. A correction can be applied for the heat lost by radiation, and this subtracted from the total loss of heat gives the heat lost by convection alone. The radiation correction was calculated from the equation

$$R = k(\theta^4 - \theta_0^4),$$

where R is the heat lost by radiation;

k the coefficient of emissivity in gram-calories per sec. per sq. cm.;

$\theta - \theta_0$ the excess of temperature of the hot cooling body above the temperature of the surroundings.

k^* was calculated from Bottomley's results to be ·63 × 10^{-12} gm.-cals. per sec. per sq. cm. for tarnished copper;

* Phil. Trans. vol. clxxxiv. p. 591 (1893).

and therefore R per cm. length

$$= k\frac{A}{l} t(\theta^4 - \theta_0{}^4),$$

A = area in sq. cms.
l = length in cms.
t = time in secs.

The values obtained are given in Table I.

TABLE I.

R (cals. per cm. length).	Diameter of Cylinder.
4 calories.	·43 cm.
12·4 ,,	·81 ,,
28·7 ,,	1·93 ,,
75 ,,	5·06 ,,
234·3 ,,	15·5 ,,
113 ,,	Stream-line Section.

It has been assumed that the temperature of the outside surface of the cooling cylinder was the same as the temperature of the steam. This is practically true, as can be shown by calculating the value of $\theta_2 - \theta_1$ from

$$(\theta_2 - \theta_1) = \frac{Hd}{2\pi rkT},$$

$\theta_2 - \theta_1$ being the drop of temperature in the tube,
H the largest value of the heat which passes across the tube per cm. length in time T,
r the mean radius = 15·4 cm.,
d the thickness = ·2 cm.,
k the conductivity of copper.

The value of $\theta_2 - \theta_1$ is ·03° C., so that the temperature of the outside of cylinder can be taken to be 100° C.

The quantity of water condensed depends on the density and the temperature of the air, so to obtain uniform results a correction was applied, and the quantity of water was reduced to a standard temperature and density.

Results.

Experiments were performed with five copper cylinders of diameters ·43, ·81, 1·93, 5·06, 15·5 cm. respectively, and the results obtained for the loss of heat in calories per cm. length (H) and the velocity (V) in metres per sec. are given in Table II.

K 2

TABLE II.
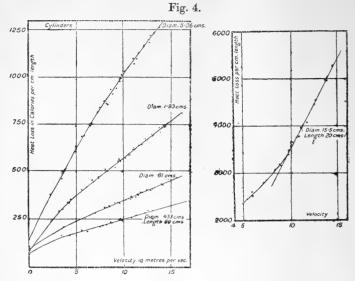
Loss of heat (H) *and Velocity* (V) *results for Cylinders.*

H = Cals. per cm. length.   R = Radiation in cals. per cm. length.
V = Velocity in metres per sec.

Cylinder (1). R=4. Diam.=·43 cm.		Cylinder (2). R=12·4. Diam.=·81 cm.		Cylinder (3). R=28·7. Diam.=1·93 cm.		Cylinder (4). R=75. Diam.=5·06 cm.		Cylinder (5). R=243. Diam.=15·5 cm.	
H.	V.	H.	V.	H.	V.	H.	V.	H.	V.
68·7	0	82·9	0	87·4	0	120·8	0	652	0
164·1	3·311	206·4	3·651	249·2	2·338	379·3	2·177	1752	3·666
166·1	4·252	279·8	7·024	292·3	3·036	461·4	3·333	2289	4·908
191·8	5·484	312·4	7·964	304·7	3·549	501·9	3·751	2451	5·396
186·6	6·148	313·6	8·248	337	4·1	602	4·776	2620	5·908
209·9	7·452	316·9	8·396	335·7	4·144	633·7	4·944	2507	5·936
216·6	7·720	315·1	8·456	354·6	4·404	686·5	5·540	2813	7·132
220·2	8·136	335·9	9·108	406·9	5·496	687·8	5·744	3081	8·284
239·8	8·668	333·7	9·496	453	6·648	736	6·380	3165	8·756
237·9	8·708	335·5	9·444	462·7	7·364	753·8	6·6	3498	9·804
		350	10·132	468·5	7·376	812·6	7·284		
		351·8	10·740	509·7	8·036				

9·824	3405	7·384	835·5	8·272	498·4	10·484	357·2	9·60	253
10·108	3659	7·832	860·8	8·336	500·1	10·872	356	9·88	243·4
10·16	3633	8·668	931	9·084	528·9	10·772	371	11·232	266·4
10·70	3766	8·752	904	9·38	553·7	11·284	364	11·376	270·3
10·94	3766	9·212	935	9·488	563·9	11·48	374·8	12·276	283·5
11·028	3974	9·576	973	9·528	554·5	11·412	376·6	12·492	292·3
11·852	4072	9·672	992	9·528	556·2	11·484	374·7	13·024	291·6
12·492	4453	9·824	1012	10·304	571·1	11·716	392·2		
12·748	4544	10·132	1033	10·492	589·2	11·916	390·9		
13·888	4974	11·048	1065	11·044	623·5	12·34	405		
14·504	5275	11·364	1096	11·064	624·1	12·836	400·3		
		11·032	1090	11·12	612	13·012	404·9		
		11·56	1124	11·604	638·6	13·224	413		
		12·036	1164	12·056	642·7	13·912	434·8		
		12·536	1192	12·3	661·7	14·088	427		
		12·78	1180	12·596	670	14·008	435·8		
		12·936	1219	12·412	672·6				
		13·204	1232	13·008	685				
		13·64	1259	13·112	692·4				
		14·312	1298	13·272	694·9				
				13·052	731				
				13·812	705				
				13·896	732·8				
				14·896					

These are also shown in curves (fig. 4), the loss of heat having been plotted against the velocity.

Fig. 4.

These curves show that the heat-loss is a function of the velocity which may approximately be represented by

$$H = kv^n.$$

In order to find the index n, $\log H$ is plotted against $\log V$, and a straight line drawn through the points. The inclination of this straight-line graph gives n.

The values of n obtained for the various cylinders are exhibited in Table III.

TABLE III.
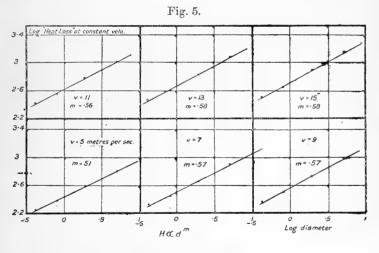
n.	Diameter.
·55	·43 cm.
·6	·81 ,,
·65	1·93 ,,
·7	5·06 ,,
·98, ·6 at low velocities.	15·5 ,,

The above table shows that n increases from ·5 for cylinders of very small diameter to 1 for cylinders of large

diameter, thus bringing into agreement the two formulæ which had been obtained by different experimenters, $H = ktv$ given by Reynolds, Nicholson, Williams for large bodies, while Boussinesq, Morris, King arrived at the formula $H = kt \sqrt{v}$ for wires. In the case of those cylinders, with which a number of readings at fairly low wind-velocities have been obtained, there are indications that the value of n is much smaller. With the cylinder of diameter 1·93 cm., n at very low velocities is ·57, while at higher velocities n is ·65; and with the large cylinder of diameter 15·5 cm. $n = ·6$ at low wind-velocities, whereas at high velocities it is ·98.

Variation of Heat-Loss with Diameter.

The way in which the heat lost varies with the diameter can be obtained by comparing the heat-loss from the different tubes at the same velocity. These values are plotted in fig. 5, and it will be seen that the heat lost is proportional to $d^{·57}$ at all velocities.

Fig. 5.

Stream-Line Section.

In several technical applications it is important that the cooling system should have as small an air resistance as possible, and accordingly a few experiments were made on a tube of stream-line section with the object of finding its efficiency for cooling purposes. The perimeter of the cross section of the tube was 23·1 cm., its maximum thickness being 2 cm.

Experiments were performed with the tube placed thus

Direction of wind.

and a third set of readings was obtained with the tube in the second position, with a metallic strip, $\frac{1}{2}$ inch in width, placed in front. This was caused to oscillate by the wind and produced irregular convection. The results are given in Table IV., and they are also shown in curves in fig. 6.

TABLE IV.
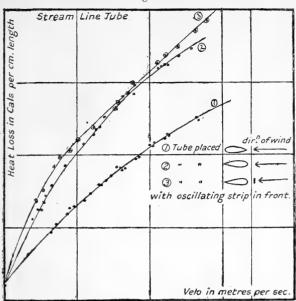
Loss of Heat (H) *and Velocity* (V) *results for Stream-Line Tube.*

H = Calories per cm. length.   V = Velocity in metres per sec.
R = Radiation corr. in cals. per cm. length = 113.

(1) Tube placed	Direction of wind.	(2) Tube placed	Direction of wind.	(3) Tube placed with oscillating strip in front.	
H.	V.	H.	V.	H.	V.
137·3	0	136·2	0	136·2	0
136·2	0	137·3	0	137·3	0
482·5	3·2512	553·1	1·912	686·7	2·285
520·6	3·6304	628·9	2·341	759	2·821
591·9	4·304	628·9	2·555	918	3·502
635·7	4·528	675·4	2·704	984	3·908
645·4	4·752	720·3	2·890	1032	4·612
680·9	5·560	795·0	3·254	1099	5·184
732·3	5·956	930	4·228		
797·3	6·576	1080	5·560	1180	6·352
793·3	6·652	1140	6·228		
823·5	7·060	1187	6·352	1317	7·856
860·1	7·292	1190	6·652	1354	7·980
917	7·780	1267	6·920	1417	8·656
903	8·016	1405	8·300	1490	9·004
889	8·160	1486	9·076	1627	10·692
898	8·420	1594	10·784	1682	11·196
966	9·216	1614	11·116	1778	12·132
973	9·360	1614	11·468	1851	13·212
1071	10·080	1610	10·928	1905	14·872
1084	10·464	1682	12·172		
1060	10·280				
1116	11·304				
1139	11·376				
1135	11·456				
1255	13·332				
1231	13·504				

Fig. 6.

The values of n obtained were :—

$$(1) \quad n = \cdot 67,$$
$$(2) \quad n = \cdot 62,$$
$$(3) \quad n = \cdot 61.$$

These results show that the heat lost from the stream-line tube is slightly greater than that lost from a circular tube of same total area, but much greater than from a circular tube of the same width or same air resistance. This will be more clearly shown by the following comparative values.

(1) Heat-loss from stream-line tube at velocity 13 metres per sec.=1735 cals. per cm. length.

(2) Heat-loss from cylinder of same diameter as the maximum thickness of stream-line tube at velocity 13 metres per sec.=695 cals. per cm. length.

(3) Heat-loss from a cylinder of the same total area (7·3 cm. diam. approx.)=1476 cals. per cm. length at velocity 13 metres per sec.

(4) Heat-loss from cylinder of the same air resistance as stream-line tube ($\frac{1}{7}$ diam.=·3 cm.) at 13 metres per sec. =233 cals. per cm. length.

The curves in fig. 6 also show that the cooling is much greater when the stream-line tube is placed in position (2)
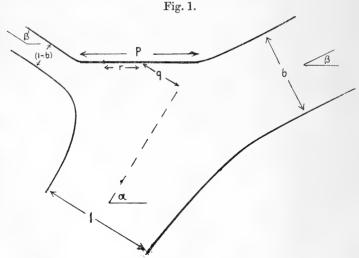
than it is when placed in position (1), and with the oscillating strip the heat-loss is increased at low and very high velocities.

It is evident, then, that as a cooling apparatus a stream-line tube is in every respect more efficient than a circular one.

The above experiments were carried out in the Physical Laboratory of the University College of North Wales, and my best thanks are due to Professor E. Taylor Jones for placing the necessary apparatus at my disposal, and to Mr. W. E. Williams, B.Sc., A.F.Ae.S., for suggesting the subject and for giving most valuable help and advice.

XVIII. *An application of Nomography to a case of Discontinuous Motion of a Liquid. By* W. B. MORTON, *M.A., and* ELEANOR J. HARVEY, *M.A., Queen's University, Belfast*[*].

THE problem of the impact, in two dimensions, of a jet of frictionless liquid on a plane strip, when both jet and strip are of finite width, can be solved by the method of conformal representation. The solution was given by Prof. Love [†]. The equations which embody the result of the analysis are too complicated to admit of arithmetical calculation of special cases. It is the purpose of this note to point out how numerical results can be obtained by means of the graphical methods developed by M. d'Ocagne.

Fig. 1.

Taking the width of the undisturbed stream before incidence as unity (fig. 1), the data of the question are the

width of the plane strip, p, the angle of incidence α, and the position of the strip with relation to the stream. This last can conveniently be specified by the perpendicular distance, q, of the middle line of the strip from the middle plane of the undisturbed jet.

The treatment of the question can be simplified by making a slight modification of the analysis as given in Love's paper. The method consists in representing on the upper half-plane of an auxiliary variable u the regions corresponding to the field of motion on the planes of $w = \phi + i\psi$ and $\Omega = -\log q + i\theta$, where $(\phi \; \psi)$ are the velocity-potential and stream-function, and $(q \; \theta)$ are the magnitude of the velocity, taken as unity on the free surfaces, and its inclination to the plane of the strip. The point $u = \infty$ is taken to correspond to the point at infinity on the incident jet, and the points $u = \pm 1$ to the edges of the strip. It is then found that $u = \cos \alpha$ corresponds to the point on the strip where the stream divides, but the variable u at other points has no simple geometrical meaning. If, however, we make $u = \infty$ correspond to the point where the stream divides, we shall find that u is $\cos \theta$ at all points on the free boundaries of the jets. Taking $u = \pm 1$ at the edges of the strip as before, the equation connecting Ω and u now becomes

$$d\Omega/du = 1/\sqrt{u^2 - 1},$$
$$\Omega = \log \{u + (u^2 - 1)^{\frac{1}{2}}\}.$$

On the free surface $u^2 < 1$ and $\Omega = i\theta$, so that $u = \cos \theta$.

The constants which appear in the analysis are the values of u which correspond to the points at infinity on the three jets. These now become the cosines of the angle of incidence α and of the "angles of splash" $\beta\beta'$ (fig. 1).

It is evident that the new variable u' is connected with the u of Love's paper by the relation

$$u' = (1 - au) / (a - u) \text{ where } a = \cos \alpha.$$

The equation giving the breadth p in terms of $\alpha\beta\beta'$ (equivalent to equation 23, *loc. cit.*) can be written in the form
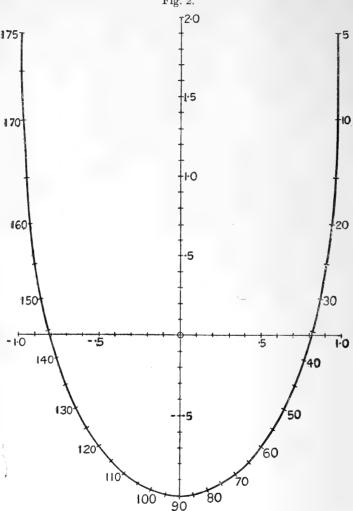
$$\begin{vmatrix} p + f(\alpha) & f(\beta) & f(\beta') \\ \cos \alpha & \cos \beta & \cos \beta' \\ 1 & 1 & 1 \end{vmatrix} = 0,$$

where $\pi f(\theta) = -\pi \sin \theta - 2 \cos \theta \log \tan \frac{1}{2}\theta.$

This suggests at once a way of finding pairs of angles $\beta\beta'$ which can be angles of splash for a stream of unit-breadth incident at angle α on a strip of breadth p.

Having plotted the curve $x = \cos \theta$, $y = f(\theta)$ (fig. 2), we can mark the point at distance p above the point α on the

Fig. 2.

Nomogram for p.

graph. Then any line drawn through this point will meet the curve in a pair of points which correspond to the angles of splash for some special setting of the lamina in the stream.

The next step is to find the value of q which corresponds to the special values of $\beta\beta'$ which have been read off on the p-nomogram.

The equation connecting q with the angles can be written in a similar form, viz. :—

$$\begin{vmatrix} q + \phi(\alpha\alpha) & \phi(\alpha\beta) & \phi(\alpha\beta') \\ \cos \alpha & \cos \beta & \cos \beta' \\ 1 & 1 & 1 \end{vmatrix} = 0.$$

This is equivalent to equation 28, *loc. cit.*, where $x_0 - \frac{1}{2}\pi \operatorname{cosec} \alpha = -(\frac{1}{2}p + q \operatorname{cosec} \alpha)\pi$. It can be represented by a nomogram as before, except that now a separate curve must be used for each angle of incidence α. The function $\phi(\alpha\theta)$, which is plotted against $\cos \theta$, has different forms according as θ is less than, equal to, or greater than α.

For

$\theta < \alpha$, $\quad \pi \cdot \phi(\alpha\theta) = -\sin(\alpha+\theta) \log \sin \frac{1}{2}(\alpha+\theta) - \sin(\alpha-\theta) \log \sin \frac{1}{2}(\alpha-\theta)$

$$+ \sin \alpha \cos \theta \log \frac{1}{2} \sin \theta + \frac{\pi}{2} \cos(\alpha-\theta).$$

$\theta = \alpha$, $\quad \pi \cdot \phi(\alpha\alpha) = -\frac{1}{2} \sin 2\alpha \log 2 \sin \alpha.$

$\theta > \alpha$, $\quad \pi \cdot \phi(\alpha\theta) = -\sin(\alpha+\theta) \log \sin \frac{1}{2}(\alpha+\theta) + \sin(\theta-\alpha) \log \sin \frac{1}{2}(\theta-\alpha)$

$$+ \sin \alpha \cos \theta \log \frac{1}{2} \sin \theta - \frac{\pi}{2} \cos(\theta-\alpha).$$

The nomograms for $\alpha = 90°$ and $\alpha = 60°$ are shown on figures 3 and 4. There is a sudden decrease, of magnitude unity, in the ordinate when θ passes the value α; the point corresponding to α is the middle point of this discontinuity. The required value of q is the distance from this point measured vertically upward to the chord joining the points $\beta\beta'$.

When the angles $\beta\beta'$ are known, the principle of conservation of momentum gives the breadths of the jets, b, $(1-b)$, into which the incident stream is split, since
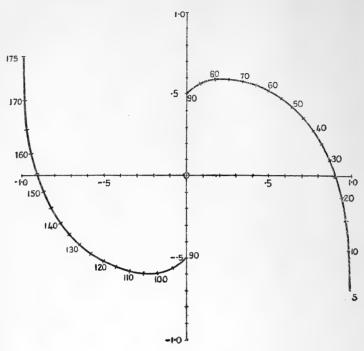
$$b \cos \beta + (1-b) \cos \beta' = \cos \sigma.$$

The same nomographic method can be used to find the position of the point on the strip at which the stream-line divides, given by its distance r from the centre of the strip (fig. 1), and also the coordinates of points on the free surfaces of the jets.

The equation for r is identical in form with the equation for p, the function now being given by

$$\pi f(\theta) = -\left(\frac{\pi}{2} - \theta\right) \sin \theta - \cos \theta \log \sin \theta.$$

Fig. 3.

Nomogram for q, $\alpha = 90°$.
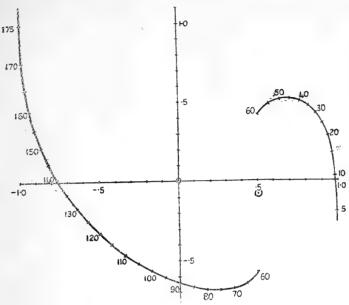
Fig. 5 shows the nomogram. It is drawn with the sign of the function reversed, so that the value of r is the distance measured *downwards* from the point α to the chord joining $\beta\beta'$.

The coordinates of a point on the free surface of the liquid are expressed as functions of the variable parameter u (equation 26, *loc. cit.*). Hence, by use of the modified analysis, we get them in terms of the inclination θ of the tangent at the point, and we find once more that the equations can be written in the nomographic form. Let the origin be at the right-hand edge of the strip, then θ runs from 0 to β along the free surface which starts from the origin, and from β to α along the other side of this jet and the right-hand side of the incident jet.

The equation for x is
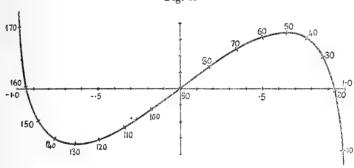
$$\begin{vmatrix} x + F(\theta\alpha) & F(\theta\beta) & \mathbf{F}(\theta\beta') \\ \cos \alpha & \cos \beta & \cos \beta' \\ 1 & 1 & 1 \end{vmatrix} = 0,$$

Fig. 4.

Nomogram for q, $\alpha = 60°$.

Fig. 5.

Nomogram for r.

where

$$\pi \cdot \mathrm{F}(\theta\chi) = \cos\chi \{\log(1-\cos\chi) - \log(\cos\theta - \cos\chi)\} \text{ when } \theta < \chi$$

and

$$\pi \cdot \mathrm{F}(\theta\chi) = \cos\chi \{\log(1-\cos\chi) - \log(\cos\chi - \cos\theta)\} + \pi\sin\chi$$
$$\text{when } \theta > \chi.$$
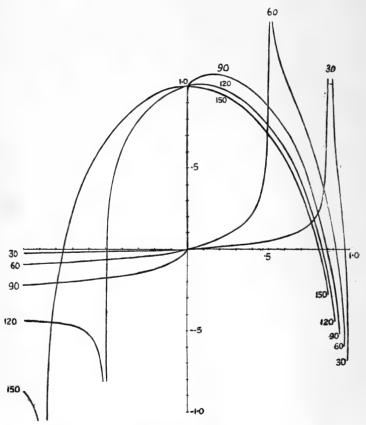
The discontinuity in $F(\theta\beta)$ when θ passes the value β gives the transit at infinity from one side of the jet to the other.

The equation for y is of the same type, the function being replaced by

$$\pi \cdot F(\theta\chi) = \sin \chi \{ \log (1 - \cos (\theta + \chi)) - \log (\cos \theta - \cos \chi) \}, \quad \theta < \chi,$$

$$\text{and} \quad = \sin \chi \{ \log (1 - \cos (\theta + \chi))$$

$$- \log (\cos \chi - \cos \theta) \} - \pi \cos \chi, \quad \theta > \chi.$$
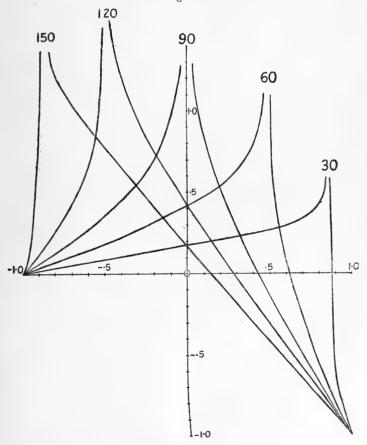
Fig. 6.

Nomogram for x.

If, now, we cover a plane with curves of the family $x = \cos \chi$, $y = F(\theta\chi)$ for different values of θ, we shall be able to read off the values of x and y respectively at points

on the surfaces of the jets where the tangent has the inclination θ corresponding to each curve. It is only necessary to join the points $\beta\beta'$ on the curve θ and find where the line meets the ordinate at the point α. It is easy to draw the boundaries of the jets when a few points have been found, because the direction of the curve at each point is known. To get the left-hand branches the origin can be shifted to the other edge and the positive direction across the strip taken from right to left, so that $\alpha\,\beta\beta'$ are replaced by their supplements.

Fig. 7.
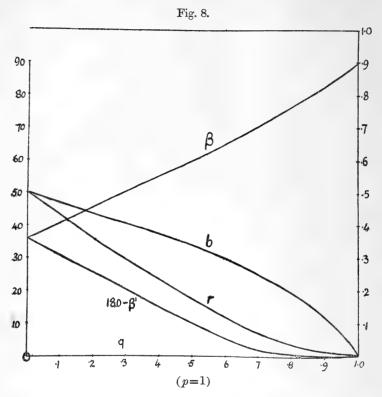
Nomogram for y.

We have drawn x and y nomograms for intervals of $10°$ in θ, but, for the sake of clearness, only the curves for multiples of $30°$ are shown on figs. 6 and 7.

Fig. 1 was drawn in this way for the case $p=1$, $\alpha=60°$, $\beta=26°\cdot3$, $\beta'=145°\cdot6$, $q=0\cdot4$, $r=0\cdot265$.

As a further illustration of the use of the nomograms, the curves on fig. 8 have been drawn for the perpendicular

Fig. 8.

$(p=1)$
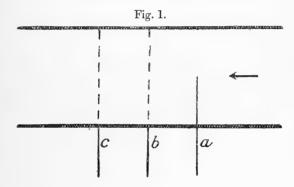
incidence of a jet on a plate of the same width. Abscissæ are distances of middle of plate from middle of jet. Angles of splash are given by the curves marked β, $180-\beta'$, using the vertical scale on the left of the diagram. The curve b gives by its distances from the top and bottom of the figure (on the right-hand scale) the parts into which the jet is divided by the plate. Curve r gives in the same way the ratio in which the plate is divided by the point at which the stream divides.

XIX. *The Production of Light by the Recombination of Ions.*
By C. D. Child[*].

IN a recent article by Strutt[†] a description is given of
experiments on the luminous vapour distilled from the
mercury arc. The conclusion is there reached that the light
given off by the vapour comes from the positive ions, while
the conclusion reached in a recent article by myself[‡] was
the opposite of this. My reasoning led to the belief that
the light does not come from either the positive or the
negative ions alone, but from the two at the time of
recombining. I desire to present the following reasons for
continuing to hold the conclusions of my previous article.

The experiment on which Strutt bases his conclusion can
be shown with the aid of fig. 1. The luminous vapour comes

Fig. 1.

from an arc at the right. *a* is an exploring wire, *b* and *c*
are iron-wire nets connected to a source of current inde-
pendent of that producing the arc. When the current passes
from *b* to *c* the region between these nets is luminous; when
it passes in the opposite direction the region is non-luminous.
Strutt believes that this is due to the presence of positive
ions in the former case and to their absence in the latter
case. He states that in the former case one-half of the
negative ions may be drawn from the field without affecting
the luminosity to an appreciable extent, and therefore the
light cannot be due to the recombination of the ions. Strutt's
reasons for believing that many of the negative ions are
taken out of this region when *b* is the anode is as follows.

[*] Communicated by the Author.
[†] Proc. Roy. Soc. A. xci. p. 92 (1914).
[‡] Phil. Mag. [6] xxvi. p. 906 (1913).

It is first shown that the region to the left of c loses its conductivity when a current is passing between b and c, showing that the ions are approximately all withdrawn from this field by the current. His further statement is as follows:—
" Using the first one b as cathode, and the wire a as anode, the current was 2·7 milliamperes. As already explained, the removal of positive ions by b was practically complete. Thus the current is a measure of the number of ions that reach this point. Next, using c as cathode and b as anode, the current was found to be diminished to 1·3 milliamperes. It follows, then, that in the absence of a field, the number of positive ions and consequently also the number of negative ones reaching c is about half the number that reach b, the remainder recombining between b and c. If, then, we make c cathode and b anode, we take out as many negative ions at b as we take out positive at c. In other words, under the particular conditions of this experiment, we take out half the entire number of negative ions that reach b, and we reduce by half the rate of recombination at this point. Yet the luminous intensity is not at all affected. It does not appear, therefore, that the luminosity can be attributed to recombination."

This argument, however, is not conclusive, since the rate of recombination is not necessarily reduced by half when the number of negative ions passing a given point is reduced by half. The rate of recombination depends on the number in a region at a given time, and this depends not only on the number passing a given point but also on their velocity after the point is passed. If, for example, the number of negative ions passing b and the velocity with which they move are both reduced one-half, then the number of ions per unit volume is not changed and the rate of recombination is the same as at first.

In reality this is what occurs in the second case suggested by Strutt. The field not only causes fewer negative ions to pass b, but it also pushes those which do pass against the flow of the gas, so that they move more slowly. Consequently the number per unit volume is but slightly changed, as will be shown in a following paragraph. To make this somewhat clearer the following conditions may be assumed. If 100 negative ions pass a we may have the following cases:—

(a) When there is no field, 50 may recombine between a and b, 25 between b and c, and 25 pass through the wire net at c ;

(b) When a is positive, b is negative, and c is uncharged,

50 ions may be drawn to a and 50 may recombine between a and b ;

(*c*) When a is uncharged, b is positive, and c is negative, 50 may recombine between a and b, 25 may be drawn to b and 25 may recombine between b and c.

We have here met all the conditions of Strutt's experiments and yet have exactly the same number of ions recombining between b and c when a current flows between those points as when there is no current. These conditions seem more reasonable when one remembers that in the first case not all of the negative ions passing a recombine between a and b, while in the second case all that pass a must somehow recombine before they reach b, since none of them go to b and none of them pass that point.

But a further consideration of the subject shows that it is not only possible that the rate of recombination is unaffected by the passage of a current, but that in the greater part of this region a condition approximating this must exist. When b is positive and c is negative the field near b is very small, as has been shown by myself (p. 908) and by Strutt (p. 94). Since the positive ions are of the same mass as the mercury atoms, this small field will give to the positive ions a velocity very much smaller than that of the stream of vapour, a velocity which has been estimated by Stark to be 28,000 cm. per sec.[*]   The same thing is apparent when we remember that the effect of the field on the positive ions must be very much less than the effect on the negative ions, and yet the effect on the negative ions is not sufficient to draw all of them against the stream of gas. That they are not all drawn out of the region is evident from the nature of the field. If a current of one milliampere were being carried by the positive ions only, a field very many times greater than that existing would be necessary.

The same number of positive ions pass b whether it is charged positively or is uncharged. If the same number passes this point and their velocity is approximately independent of the field, then the number of positive ions per unit volume is also approximately independent of the field.

But the number of negative ions per unit volume is very approximately the same as that of the positive ones, otherwise the potential difference between b and a point 1 cm. from it would be much more than that which the experiment shows. If, for example, we were to assume a current of ·06 milliampere per sq. cm., a velocity of the positive ions

of 28,000 cm. per sec. (the velocity of the stream of vapour), and that one per cent. of the current was carried by an excess of positive ions over negative ions, there would be a drop in potential between b and a point 1 cm. from it of 14·5 volts*. In a repetition of the experiment described in my previous article I found that with a current of ·06 milliampere the difference in potential between b and a point 1 cm. toward the cathode was somewhat less than 1 volt. In this experiment the total potential difference between the electrodes was 70 volts, and the distance was 1·1 cm.

We are therefore justified in saying that the number of negative ions per unit volume is very approximately the same as that of the positive ions. Therefore, the number of both positive and negative ions in the vicinity of b is independent of the current. Therefore, the rate of recombination in this region is independent of the presence of a field, and the assumption that the light is due to the recombination is entirely reasonable.

This reasoning does not hold in the immediate vicinity of the cathode, for there the change in the electric force is rapid. However, in that region the gas is not luminous when a field is applied between b and c. Consequently the conditions in that region are also quite in harmony with the idea that the light is due to recombination.

It should be noted that the preceding discussion does not claim that all light is produced by recombination. If, as has been found by Strutt, the luminous vapours rising from arsenic and antimony arcs are not affected by the electric field, there is no reason to think that such light is produced by the recombination of ions, but such an experiment would prove equally well that this light does not come from positive ions, for we could not have the negative ions drawn out and the positive ones left without the very great electrostatic effects which have been discussed in the preceding paragraphs. If this experiment with arsenic is an argument against the idea that the light in the mercury vapour is produced by recombination, as Strutt believes it is, it is equally an argument against his idea that the light in the mercury vapour is due to the vibration of positive ions.

It is, however, quite unnecessary to draw such a conclusion from this result. If the light from arsenic and antimony vapours does not behave in an electric field in the same way as that from mercury and sodium vapours, it seems more reasonable to assume that the light is produced by some different mechanism.

* Phys. Rev. xii. p. 79 (1901).

I have, therefore, in what has preceded shown that it is possible that the light produced by the vapour rising from the mercury arc is due to the recombination of ions. If it is possible to hold this view, it is more reasonable to do so than to adopt the seemingly impossible assumption that the positive ions remain luminous for ·001 sec. Strutt has shown even more clearly than was shown in my previous article the difficulty of such an assumption, and while it may be possible to imagine some mechanism of the atom which would allow this to occur, any reasonable explanation of the phenomena is preferable. I believe, therefore, that in the case of mercury vapours the assumption that light is produced by recombination is to be preferred.

Colgate University, U.S.A.,
August 1915.
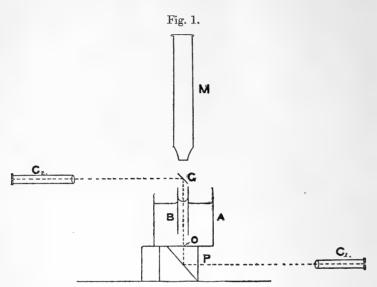
XX. *On a Method of measuring Surface-Tension and Angles of Contact.* By Prof. A. ANDERSON, *M.A., and* Mr. J. E. BOWEN, *M.A.*[*]

THE following paper gives a method, with some preliminary results, of measuring the surface-tensions of liquids and their angles of contact with glass which we have been unable to find described elsewhere. The method depends on the measurement by optical means of the radius of curvature of the meniscus in a tube immersed in a vessel of the liquid and the height of the centre above (or below) the surface of the liquid outside. It is thus freed from any correction due to the mass of the meniscus and any uncertainty as to whether the liquid actually wets the glass. The curve connecting the radius of curvature thus determined and the radius of the tube at the top of the meniscus, for a number of tubes of different diameters, enables the angle of contact to be determined.

The method will easily be understood by referring to fig. 1. A is a glass vessel with plane sides and base, O is a mark on the base, and the tube B is placed vertically so that O is on its axis produced. This was done, the tube being held in a clip attached to a ball-and-socket joint, by the aid of the microscope M, using a low-power objective. The microscope was one of the Bailey & Smith design, and moved horizontally and vertically, being provided with verniers reading to $\frac{1}{100}$ mm. The microscope is now focussed on O

and the vernier read. The liquid is then poured into the
vessel and takes up a position somewhat as shown in the
figure : in these preliminary readings, in order that all our
readings for each tube might be taken with the apparatus in

Fig. 1.

position, it was usual in the case of liquids which rise in
tubes to fill the tube to the top and then take out a little of
the liquid from the vessel until the top of the meniscus is
just below the top of the tube; the radius of the tube at the
top was then taken as the radius at the top of the meniscus.
The microscope is now focussed upon the image of O
formed by refraction at the meniscus, and finally upon the
centre of the meniscus. The three readings give u and v the
distances of the object and image from the centre of the
meniscus, and from the formula

$$\frac{1}{v} - \frac{\mu}{u} = \frac{\mu - 1}{R},$$

where μ is the refractive index of the liquid, the radius of
curvature R at the centre of the meniscus can be found.
The meniscus being a surface of revolution the curvature of
any vertical section is the same, hence

$\dfrac{2T}{R}$ =the difference of pressure on the two sides $= g\rho h$,

where h is the height of the centre of the meniscus above the level of the liquid in the vessel A. h was found by moving the microscope horizontally and focussing on the surface of the liquid. Thus T may be found without applying any corrections.

In order to get rid of one of the observations parallel light was used instead of using the mark O. A prism P with angles $90°$, $45°$, $45°$ was fixed with Canada balsam to the bottom of the vessel A, and parallel light from the collimator C_1 was directed up the centre of the tube. In this case $u = \infty$ and $R = (\mu - 1)v$, so that only the three readings corresponding to v and h need be taken. Here $T = g\rho h R/2 = \frac{1}{2}g\rho(\mu - 1)hv$. Thus since $hv = \text{const.}$ the best conditions for working are those in which $h = v$, or a tube should be chosen which gives a capillary rise in the neighbourhood of $\sqrt{2T/g\rho(\mu-1)}$.

The following rough readings show the result for water with tubes of different diameters.

Radius of Tube. r (in cm.).	Radius of Curvature. R (in cm.).	Surface-Tension. T.
·386	·507	70·6
·318	·378	71·3
·212	·230	70·8
·123	·124	70·7
·09	·092	71·2

The objection to the method as described above is that it is always difficult and in some cases (*e. g.* turpentine) impossible to be sure of focussing on the centre of the meniscus. To do away with the necessity for focussing on the meniscus, another image, this time by reflexion, was formed. Light from a second collimator, C_2, fell upon a piece of glass, G, with parallel sides (a microscope-slide cover was found to work excellently) placed at an angle of $45°$ with the axis of the tube, whence it was reflected down to the surface of the meniscus, which formed an image on the axis of the tube at a distance $R/2$ from the centre of the meniscus: all readings through the microscope must be taken through the plate G. Thus, if d be the difference between the vernier readings

corresponding to the refracted and reflected images,

$$d = \frac{R}{2} + \frac{R}{\mu - 1},$$

$$R = \frac{2(\mu - 1)}{\mu + 1} \cdot d,$$

and R is found without focussing on the meniscus. The position of the meniscus centre may easily be got from the reading of the reflected image by subtracting R/2. The above method was tested by readings with olive oil, the surface of which can generally be focussed on, by calculating the position of the surface of the meniscus, and also getting it by direct focussing : the results agreed to a high degree of accuracy. It is obvious that for opaque liquids (*e. g.* mercury) this reflexion method can be used to find the radius of curvature of the centre of the meniscus provided the surface can be accurately focussed on.

The following tables give a series of readings with tubes of different diameters for olive oil and mercury. As the surface-tension of mercury varies considerably, freshly distilled mercury was not used, but clean mercury which was filtered through a pin-hole in a paper funnel before each reading. This was done as we wished to keep the mercury in as far as possible the same condition in order to test the method of finding angles of contact, mercury being the only liquid whose angle of contact is known to any degree of accuracy. The readings with the narrower tubes in the case of mercury could not be taken exactly as described owing to the meniscus being so far below the surface in the vessel, so with these a piece of the tube was sealed to a wide-mouthed funnel and then bent in **U**-shape until the end of the tube was slightly below the top of the funnel : the readings were then easily taken.   *r*, R, and *h* are given in cm., T in dynes per cm.

Olive Oil.

r.	R.	*h.*	T.
·328	·460	·155	32·2
·222	·267	·269	32·4
·155	·162	·441	32·2
·045	·045	1·592	32·3

Mercury.

r.	R.	h.	T.
·382	·822	·073	400
·215	·316	·189	398·2
·156	·214	·279	398
·056	·074	·808	398·6

The values found for the surface-tensions of glycerine and turpentine were :—

$$\begin{array}{lll} \text{Glycerine} & . \quad . \quad . \quad . \quad . & 65·1 \\ \text{Turpentine} & . \quad . \quad . \quad . \quad . & 27·2 \end{array}$$

All the above readings were taken at a temperature of approximately 16°. The glass vessel and tubes were cleaned with concentrated sulphuric acid, caustic potash, and alcohol, being washed between each two in running water, and finally dried and immersed in the liquid to be used.

To apply the method to finding angles of contact it is only necessary to remark that, either from an approximate solution of the equation to the capillary surface (see Ferguson, Phil. Mag. July 1914) or by assuming the meniscus to be spherical in the limit, it follows that $\lim_{r \to 0} r/R = \cos \theta$, where θ is the angle of contact. Thus if we plot values of r as abscissæ and values of R as ordinates, we get a curve the inclination of the tangent to which at the origin is $\tan^{-1} (\cos \theta)$. If the tangent makes an angle of 45° with the axis of x, the value of θ is 0° and the liquid may be truly said to wet the tube.

The following tables give readings of r and R for glycerine and turpentine respectively :—

Turpentine.   Glycerine.
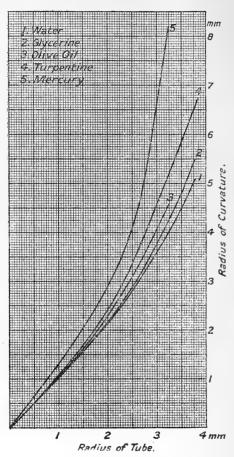
r.	R.	r.	R.
·385	·674	·385	·549
·247	·341	·247	·284
·162	·178	·154	·16
·128	·137	·09	·093
·09	·093	·038	·038₂
·038	·038		

The curves (fig. 2) were obtained by plotting r against R for water, glycerine, olive oil, turpentine, and mercury.   It will

Fig. 2.

be noticed that all appear to approach the origin at an angle of 45° with the exception of mercury. This points to a zero angle of contact with all except mercury. Mercury gives an angle of nearly 41°, or rather, a little greater than $180° - 41° = 139°$.

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XXI. *The Complete Photoelectric Emission*[*]. *By* Professor O. W. Richardson, *F.R.S.*, *Wheatstone Professor of Physics, University of London, King's College*[†].

IT is well known that when light of sufficiently short wave-length is allowed to fall on metals, an emission of electrons takes place under its influence. Since all substances emit light when they are raised to a high temperature, an emission of electrons from hot bodies owing to the action of light will occur even when they are not illuminated from an external source. The emission of electrons which arises in this way may conveniently be termed the "complete photoelectric emission," to indicate that it is excited by the complete (black body) radiation with which the material is in equilibrium at the temperature under consideration. It is of interest to enquire whether this emission will resemble in its behaviour the thermionic effects which have been investigated experimentally, and to seek to determine how its magnitude compares with that of the observed thermionic emission.

The most striking property of the thermionic emission of electrons is that expressed by the current temperature relation

$$i = A T^\lambda e^{-b/T} \quad \ldots \quad \ldots \quad (1)$$

(i = maximum current from unit area, T = absolute temperature, A, λ, and b constants). The writer[‡] has shown that it follows from simple thermodynamic considerations that the complete photoelectric emission is also governed by an equation of type (1)[§]. The thermodynamical argument does not determine the numerical value of the constants A and b (λ is unimportant) which enter into the formula for the complete photoelectric emission. It does, however, determine the meaning of b, which is closely related to the work done by an electron in escaping from the metal. The values of the minimum frequency of the light which is able to excite any photoelectric emission from metals show that b is not very different in the case of photoelectric and thermionic emissions from a given material. It is not

certain that the values of b for the two effects are not identical for the same substance. The value of A, on the other hand, is left entirely arbitrary by the thermodynamic considerations, which do not therefore enable us to determine the scale of magnitude of the complete photoelectric emission. Thus the theoretical argument leads us to the conclusion that the complete photoelectric emission varies in the same general manner with temperature as the observed thermionic effects: it is possible, although not certain, that the indices λ and b are identical in the two cases contrasted, in which case the two emissions would be in the same relative proportion at all temperatures ; on the other hand, the absolute value of the complete photoelectric emission is left entirely undetermined, so that we are unable to determine by such calculations what proportion it bears to the observed thermionic emission.

This information can, however, be obtained from known photoelectric data in the case of the metal platinum. The calculations are not exact, but it is improbable that the sources of uncertainty in the calculations will lead to errors in the final results which are as great as those pertaining to the experimental measurements of the absolute values of photoelectric and thermionic emissions from a given material. Data* now available give the number of electrons emitted from certain metals, including platinum, when unit light energy of the different effective frequencies falls on them at normal incidence (or at some other angle which is definitely specified). The magnitude of the complete photoelectric emission will not, however, be obtained if we simply multiply this number by the corresponding intensity of the light in the black-body spectrum and integrate the product over the whole range of frequency, on account of the different optical conditions in the two cases. In the photoelectric experiments in which a beam of light is incident normally, the intensity of the exciting illumination is greatest at the surface and falls off exponentially as the depth of penetration increases. In the natural emission, on the other hand, the electromagnetic radiation is isotropic, and its intensity is the same at all depths. This particular difference between the two cases can be allowed for if we have a knowledge of the coefficients of absorption of the electromagnetic radiations of different wave-lengths and of the electrons which they cause to be emitted.

It is usual to assume that both the light and the electrons

* Richardson and Rogers, Phil. Mag. vol. xxix. p. 618 (1915).

are absorbed according to an exponential law, although such
an assumption can be regarded as only a very rough kind
of approximation when applied to the very slowly moving
electrons with which we are now dealing. In reality the
problem involved here is a very complex one : the stream of
electrons which travels in a given direction is depleted in
number both through the electrons being stopped and through
scattering, and it also suffers loss of energy. Little is known
definitely either as to the relative importance or as to the
precise effect of these different actions. In addition, the
electrons which escape lose most of their energy in passing
through the surface ; although this fact need not prevent
their absorption being approximately exponential when they
are travelling in the interior. In any event, the exponential
law of internal absorption is the only assumption with which
it is possible to arrive at any result in the present state of the
subject.

Consider first the case of a beam of light of definite
frequency incident normally, and let I be the energy crossing
unit area just within the surface of the metal in unit time.
Of the electrons ejected from atoms in a layer of infinitesimal
thickness perpendicular to the beam, let the proportion e^{-ax}
reach a parallel plane at a distance x from the layer. Let β
be the coefficient of absorption of the light and N the
number of electrons ejected from the atoms of the metal when
unit energy is absorbed by them from the light. A calcu-
lation following well-known lines, which allows for the
absorption of both light and electrons in accordance with
the assumptions just indicated, shows that the number N_1 of
electrons which reach unit area of the surface bounding the
metal in unit time is given by

$$N_1 = \frac{\beta I}{\alpha + \beta} N. \quad \cdots \quad \cdots \quad (2)$$

We assume that a definite fraction, γ, of these escape from
the surface. In general γ will be a function of the frequency
of the light, and will be different for different materials.

Using Planck's notation, the intensity $i_\nu d\nu$ of the isotropic
natural radiation inside the material, within the frequency
range from ν to $\nu + d\nu$, is

$$i_\nu d\nu = 2 \frac{r^2}{c^2} \frac{h\nu^3 d\nu}{e^{h\nu/kT} - 1}, \quad \cdots \quad \cdots \quad (3)$$

where r is the real part of the complex refractive index of
the material. A calculation similar to that leading to (2)

except for the fact that the intensity of the radiation is now constant at different depths, shows that this radiation delivers at each unit area of the surface in unit time the number $N_2 d\nu$ of electrons, where

$$N_2 d\nu = 4\pi N \frac{\beta}{\alpha} i_\nu d\nu = 4\pi \frac{N_1}{I} \frac{\alpha + \beta}{\alpha} i_\nu d\nu, \quad . \quad . \quad (4)$$

from (2). This method of calculating assumes that the liberation of electrons from the atom by light is a consequence solely of the absorption of the light and is not a result, for example, of the process of emission of light. The total number of electrons which escape is obtained by multiplying this by the factor γ and integrating throughout the spectrum. The complete photoelectric emission current J is therefore equal to

$$J = \int_0^\infty \epsilon \gamma N_2 d\nu = \frac{8\pi\epsilon}{c^2} \int_0^\infty \frac{\alpha + \beta}{\alpha} \frac{\gamma N_1}{I} r^2 \frac{h\nu^3}{e^{h\nu/kT} - 1} d\nu. \quad . \quad (5)$$

For any particular temperature T, the integral on the right-hand side of (5) can be evaluated graphically if we know β/α, r, and $\gamma N_1/I$ for all frequencies.

In the case of platinum, values of $(1-\rho) \dfrac{\gamma N_1}{I}$ for all frequencies for which the factor $h\nu^3/(e^{h\nu/kT} - 1)$ is appreciable have been given by Richardson and Rogers[*]. In this expression ρ is the reflexion coefficient from platinum at normal incidence for light of frequency ν. This quantity has only been measured over part of the effective spectrum, but the data given by W. Meier[†], which extend as far as $\lambda = 2\cdot57 \times 10^{-5}$ cm., show that we shall not go far wrong if we take ρ as having an average value $1/3$ over the region under consideration. This region extends from $\lambda = 1\cdot9 \times 10^{-5}$ cm. to $\lambda = 2\cdot75 \times 10^{-5}$ cm. approximately, the effective average value of λ being in the neighbourhood of $2\cdot46 \times 10^{-5}$ cm. Data also given by Meier[†] show that the effective average value of r^2 can be taken to be not far from $1\cdot3$ over the same region. The only datum bearing on the relative values of α and β is an observation by Rubens and Ladenburg[‡], who found that when ultra-violet light passed through a thin gold leaf the emission of electrons from the front side was 100 times as great as from the side of emergence, whereas the intensity of the incident light was 1000 times that of the emergent

[*] *Loc. cit.*
[†] *Ann. der Physik*, vol. xxxi. p. 1027 (1910).
[‡] *Ver. der deutsch. Phys. Ges.* ix. p. 749 (1907).

light. From these numbers Partzsch and Hallwachs *
have calculated that for gold $\alpha = 1 \cdot 03 \times 10^6$ cm.$^{-1}$ and
$\beta = 0 \cdot 59 \times 10^6$ cm.$^{-1}$. Since gold and platinum do not differ
much from one another in atomic weight and density, the
value of the electron absorption coefficient α will almost
certainly be much the same for both metals. Meier's katoptric
measurements with gold at wave-length $\lambda = 2 \cdot 57 \times 10^{-5}$ give
numbers which lead to $\beta = 0 \cdot 56 \times 10^6$ cm.$^{-1}$, in satisfactory
agreement with that deduced from Rubens and Ladenburg's
observation. The absorption coefficient for platinum in this
part of the spectrum is larger than that for gold in the ratio
1·65 to 1·14 according to Meier ; so that in dealing with
platinum the value of β should be increased to $0 \cdot 85 \times 10^6$ cm.$^{-1}$
instead of $0 \cdot 59 \times 10^6$ cm.$^{-1}$. In this way we estimate the
value of $(\alpha + \beta)/\alpha$ over the part of the spectrum which is
photoelectrically active to be

$$(\alpha + \beta)/\alpha = 1 \cdot 82. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In arriving at the value of the complete photoelectric
emission from platinum at 2000° K. the product $\dfrac{(\alpha + \beta) r^2}{\alpha(1 - \rho)}$
has been taken outside the integral in (5) and the foregoing
average values substituted in it. This is not exact, but it
is the best that can be done with the data at present available,
and in any event it is accurate enough for the immediate
purposes of these calculations. The remaining integral
$\displaystyle\int_0^\infty (1 - \rho) \dfrac{\gamma N_1 e}{I} \dfrac{h\nu^3}{e^{\frac{h\nu}{kT}} - 1} \, d\nu$ has then been evaluated graphically,
using the values of $(1 - \rho) \dfrac{\gamma N_1}{I} \epsilon$ given by the measurements
of Compton and Richardson† and Richardson and Rogers‡.

It is not claimed that the results of these calculations give
more than a rough idea of the magnitude of the complete
photoelectric emission. For one thing, the absolute value
of the photoelectric emission when measured under a given
illumination varies considerably with the state of the metal
surface, and in a manner which cannot be said fully to be
understood. In the second place, a number of approximate
or doubtful assumptions are involved in the calculations. Of

* *Ann. der Physik,* vol. xli. p. 269 (1913).
† Phil. Mag. vol. xxvi. p. 549 (1913).
‡ *Loc. cit.*

these, the uncertainty as to the exact law of absorption of the electrons inside the metal and the approximation involved in taking certain factors outside the integral have already been alluded to. In addition, it is likely that γ will be a little different for the electrons liberated by light of a given frequency when isotropic and when incident normally. It is, however, quite improbable that any of these considerations can introduce erroneous factors large enough seriously to affect the order of magnitude of the final result.

Proceeding in the way indicated above, it appears that the value of the complete photoelectric emission current density for platinum at $2000°$ K. should be

$$i = 2 \cdot 1 \times 10^{-11} \text{ amp. per cm.}^2 \quad . \quad . \quad . \quad (7)$$

Let us now compare this value with the observed thermionic electron emission for platinum at the same temperature. In considering these questions platinum has been used because it is the only element for which the requisite photoelectric, thermionic, and optical data are available. There is one further point. The value (7) has been obtained on the assumption that the hot body is in an enclosure surrounded by radiation in equilibrium with it at its own temperature. This condition is not satisfied in the thermionic measurements. Most of the electromagnetic radiation emitted by the hot body never returns to it. The radiation density inside the hot body will thus be something less than that assumed in calculating the value (7). Thus (7) is to be regarded, subject to the limitations as to accuracy already referred to, as an upper limit to the photoelectric contribution to the electron emission from the hot body.

The following values of the thermionic current densities at $2000°$ K. from a number of elements, including platinum, have been found by Langmuir under very good conditions as to freedom from gaseous contamination:—

Element ....→	W.	Ta.	Mo.	Pt.	C.
Thermionic current (amp. per cm.²). →	3×10^{-3}	7×10^{-3}	13×10^{-3}	6×10^{-4}	10^{-3}

These are enormously greater than the value (7) of the complete photoelectric emission calculated for platinum at this temperature. The smallest thermionic currents from platinum ever recorded in the neighbourhood of $2000°$ K.

are those observed by H. A. Wilson* with well oxidized wires. He found 4×10^{-8} amp. per cm.² at 1686° C., which corresponds to nearly 10^{-7} amp. per cm.² at 2000° K. Even in this extreme case the observed thermionic current is about 5000 times as large as the complete photoelectric current.

We are thus led to the conclusion that the complete photoelectric emission gives rise to an insignificant portion only of the observed thermionic currents. While this conclusion cannot be held to be established with absolute certainty, on account of the doubtfulness of some of the factors entering into the calculations, it does, nevertheless, appear extremely probable on the evidence. In view of its importance, it is desirable that the question should be settled quite definitely; but it is questionable whether any considerable advance on the present calculations can be effected without a material extension of our knowledge of the conditions involved in photoelectric action.

If photoelectric action had proved successful in accounting completely for thermionic emission of electrons, one would have been tempted to speculate further, and to ask whether ordinary evaporation—the emission of uncharged molecules instead of charged electrons—might not be attributable in a similar way to the direct action of radiation. One could imagine the emission of molecules in evaporation to be the result of a kind of photo-chemical action, the effective radiations being mainly in the infra-red. Such a position would obviously be in line with current ideas as to the nature of heat-energy which are based on the quantum hypothesis. It is not improbable that certain radiations may be found to have a selective and direct effect in increasing evaporation, in addition to the quite obvious but less direct effect due to the heat generated by the absorption of the radiation ; and this effect is worth looking for. But judging from the analogy with the relation between ordinary photoelectric action and the emission of electrons from hot bodies, it seems likely that such effects, if they exist, will account for only a small fraction of the emission of molecules in ordinary evaporation.

* Phil. Trans. A. vol. ccii. p. 262 (1903).

XXII. *The Quantum of Action.* By WILLIAM WILSON, *Ph.D., Lecturer in Physics, University of London, King's College* *.

IN a recent paper on the Quantum Theory †, Jun Ishiwara starts out from an assumption which closely resembles an hypothesis published by me about the same date ‡. The aim of Ishiwara's theory also appears to be the same as that of mine—namely, to furnish a common basis on which the theory of complete (black body) radiation, spectral series, and other phenomena can be established. It is therefore desirable that the two hypotheses should be compared and the differences between them clearly pointed out.

Ishiwara's assumption may be stated as follows :—

"Let $q_1 q_2 \ldots q_j$ and $p_1 p_2 \ldots p_j$ be the positional and impulse coordinates of an elementary material system in a state of steady periodic motion, or of a system consisting of a very large number of elementary systems in statistical equilibrium, and let each pair, q_i, p_i, be represented by rectangular coordinates in a plane ; then the motion of the system is such that we may divide each plane into regions of 'equal probability,' whose mean value, for any state of the system,

$$\frac{1}{j} \sum_{i=1}^{i=j} \int p_i \, dq_i = h$$

is a universal constant " §.

The hypotheses which I have proposed as a foundation for the Quantum Theory are stated at some length in the paper mentioned above ‖, and may be put rather more shortly in the following form :—

(1) Each dynamical system behaves as a conservative one during certain intervals, and between these intervals are relatively very short ones during which definite amounts of energy may be emitted or absorbed.

(2) The motion of a system in the intervals between such discontinuous energy exchanges is determined by Hamiltonian dynamics as applied to conservative systems. We may speak of a system, during such an interval, as being in one of its steady states.

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(3) The discontinuous energy exchanges always occur in such a way that the steady motions satisfy the equations :—

$$\int p_1 \, dq_1 = \rho h$$
$$\int p_2 \, dq_2 = \sigma h$$
$$\int p_3 \, dq_3 = \tau h$$

. . . .

where ρ, σ, τ, ... are positive integers (including zero) and the integrations are extended over the values of q_i, p_i corresponding to the period $\frac{1}{\nu_i}$. The factor h is a universal constant.

Here also we may represent each pair q_i, p_i by rectangular coordinates in a plane, and it is a consequence of the third hypothesis that the state of any system, at any given time, will be represented by a point on a certain locus in each q, p plane. These loci divide all the planes into *equal* areas,

$$\iint dp \, dq = h.$$

This third hypothesis is clearly very different from Ishiwara's, though it is obvious that it will lead to similar and, in some cases, identical consequences. The essential differences between the two assumptions are :—

(*a*) When a large number of systems are in statistical equilibrium their representative points are, in Ishiwara's theory, uniformly distributed through any region in a q, p plane. These regions have not necessarily equal areas, but the mean area of the regions in which the representative points of any one system are situated is equal to the universal constant h. In my theory each q, p plane is divided into regions of equal area, and the representative points of a system are always on the boundaries between these regions.

(*b*) Another distinction between the two theories is connected with the limits of the integral

$$\int p \, dq.$$

Ishiwara extends the integration over the whole period of motion of the system, whereas in my theory it is extended over the period corresponding to the coordinate concerned.

A short critical discussion of the various forms of Quantum Theory, especially those of Planck, Ishiwara, Bohr, and that recently put forward by me, will not be

out of place here. Regions of "equal probability" consti-
tute a feature of Planck's later theory and that of Ishiwara.
The essentials of Planck's theory, which appears to me to be
included as a special case in that of Ishiwara, can be very
shortly stated. He deals with a very simple type of system,
the equation of motion of which is

$$m \frac{d^2q}{dt^2} + \mathrm{K}q = 0$$

when it is in a steady state, *i.e.* neither emitting nor
absorbing energy. We easily deduce the following relation
between p and q :—

$$\frac{p^2}{(2\pi m\nu\mathrm{A})^2} + \frac{q^2}{\mathrm{A}^2} = 1,$$

where $p = m\dfrac{dq}{dt}$, A is the amplitude of the motion, and ν the
frequency. This is the equation of an ellipse. For different
amplitudes we have a number of similar and similarly
situated ellipses, and it can be shown in a very simple way
that the energy of the system, or oscillator, is equal to

$$\mathrm{H}\nu,$$

where H is the area of the corresponding ellipse. This
result is obtained by the use of the principles of ordinary
dynamics. If, now, we suppose the oscillators to be capable
of interchanging energy with one another, and proceed to
investigate, by the same principles, the law of their distribu-
tion throughout the q, p plane, under statistical equilibrium,
we assume the distribution to be uniform in an infinitesimal
region

$$dp\, dq = d\mathrm{H},$$

and write

$$d\mathrm{N} = \mathrm{N}f\, dp\, dq,$$

where N is the number of oscillators and $d\mathrm{N}$ the number in
the region $dp\, dq$. We readily find

$$f = \frac{\nu}{k\mathrm{T}} e^{-\frac{\mathrm{H}\nu}{k\mathrm{T}}} \,*,$$

where H is the area of the ellipse on which the element
$dp\, dq$ is situated and k is the "gas constant" reckoned for
one molecule. This result may be called the Maxwell law
of distribution. It leads to the conclusions, (*a*) that the

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* We are assuming, as Planck does, that the directions of vibration
are perpendicular to a fixed plane, and that the oscillators are fixed.

average energy of an oscillator is kT, and (*b*) the Rayleigh-Jeans law when equilibrium is established between the oscillators and the æther. These conclusions not being in accord with experimental facts, Planck has recourse to the following main hypothesis. He supposes the oscillators to be uniformly distributed through a finite (not infinitely small) region

$$H' - H = h,$$

bounded by two of the ellipses mentioned above. The whole of the q, p plane is thus divided into areas each equal to h. These are his regions of " equal probability." It is now seen that the area of any ellipse separating two such regions can be expressed in the form

$$\int p \, dq = (n+1)h,$$

where n is any positive integer (including zero) and the average energy of the oscillators in the region is

$$\overline{E}_n = (n + \tfrac{1}{2})h\nu.$$

The law of distribution is now

$$f = (1 - e^{-\frac{h\nu}{k\mathrm{T}}})e^{-\frac{nh\nu}{k\mathrm{T}}},$$

where f is the fraction of the total number of oscillators situated in the region n. The average energy of all the oscillators is

$$\overline{E} = h\nu \left(\frac{1}{2} + \frac{1}{e^{\frac{h\nu}{k\mathrm{T}}} - 1} \right).$$

There are, in my opinion, objections to the hypothesis of regions of " equal probability." It appears to involve energy exchanges of a continuous character side by side with discontinuous exchanges. Indeed, Planck assumes [*] that his oscillators absorb energy in accordance with ordinary dynamical laws, but emit it in a discontinuous manner. So long as no other way of accounting for the phenomena concerned can be found, such hypotheses may be justifiable ; but no theory can be held to be satisfactory which applies one system of dynamics to the process of absorption and another to that of emission. This, however, is what is done in the theories of Planck and Ishiwara [†]. Moreover, there is at least one consequence of the continuous absorption hypothesis which is not in good accord

[*] M. Planck, *Theorie der Wärmestrahlung*, p. 150, 2nd Edition.

[†] *Cf.* Jeans, "Report on Radiation and the Quantum Theory," Phys. **Soc.** 1914, p. 82.

with experimental results. It demands a photo-electric "accumulation period." The experiments of Marx and Lichtenecker* seem to show, however, that this period (if it exists at all) must be much shorter than that calculated from the principles of Planck and Ishiwara.

The later theory of Planck and that of Ishiwara are not, and cannot be, extended to æther vibrations, since such an extension would involve the consequence that the æther would possess energy at the absolute zero of temperature. In fact, Planck, in developing his theory, has been at some pains to leave the æther within the domain of ordinary dynamical methods. In consequence of this, he is forced to load his theory with a highly arbitrary additional hypothesis connecting the probability of an emission of an oscillator and the intensity of the radiation of like frequency in its neighbourhood†.

These objections cannot be advanced against the form of Quantum Theory I have suggested, while it has the advantage over those of Planck, Ishiwara, and Bohr that only one hypothesis is used which goes beyond ordinary dynamics. This is the hypothesis (3) stated above, which lays certain restrictions on the interchange of energy between material systems and between such systems and the æther. It is not claimed that this hypothesis goes far enough, or that it is sufficiently complete to lead in all cases to unambiguous results; but it leads, I believe, to all those results of the other theories mentioned which are in agreement with experimental facts. Some of these have been dealt with in my previous paper ‡. It leads to Einstein's law without requiring an "accumulation period." This can be shown in the following way :—The average energy of the vibrations in the illuminated solid is given by

$$\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1},$$

if we only consider vibrations perpendicular to a fixed plane. Now, for the whole range of temperatures within which photo-electric measurements have been made, and for values of ν in the ultra-violet or even in the visible part of the spectrum, this expression reduces to an exceedingly small fraction of $h\nu$. Most of the vibrations therefore in this range of frequencies have no energy at all. The number having the energy of $h\nu$ will be a very small fraction of the

* E. Marx & K. Lichtenecker, *Ann. d. Phys.* xli. p. 124 (1913).

† M. Planck, *loc. cit.* p. 159.

‡ W. Wilson, *loc. cit.*

total number, and for systems having the energy $2h\nu$ the fraction belongs to the second order of small quantities. It follows therefore that in all but a very small number of cases the energy emitted must be equal to $h\nu$, and if an emission is accompanied by the ejection of an electron, its kinetic energy cannot exceed this value.

A very important consequence of hypothesis (3), to which I wish to draw attention here, is that any emission of energy of frequency ν to the æther must be equal to

$$n h \nu,$$

where n is an integer. Such considerations as those in the last paragraph lead to the conclusion that n must be unity for frequencies in the visible range of the spectrum and for higher frequencies. This result appears in the theories of Bohr and Ishiwara as a special assumption which cannot be deduced from the other hypotheses they adopt.

Any form of Quantum Theory must involve assumptions intimately connected with physical quantities having the dimensions of an action, and the most important of these is angular momentum. The hypothesis (3) given above makes the angular momentum of a system equal to

$$\frac{nh}{2\pi}$$

(where n is an integer), even in the case of an electron the orbit of which is elliptical *. This is not inconsistent with Bohr's hypotheses, and coincides with his views in the case where the ellipse degenerates into a circle. The assumption (3) lays certain restrictions on the possible values of the eccentricity of the electron orbit. This can be shown as follows :—Let q_1 represent the distance of the electron from the nucleus and q_2 its angular distance from a suitably chosen fixed line. Then we have for the equation of the ellipse

$$q_1 = \frac{B}{1 + e \cos q_2},$$

and therefore

$$p_1 = \frac{p_2 e}{B} \sin q_2,$$

and

$$\int p_1 \, dq_1 = p_2 e^2 \int_0^{2\pi} \frac{\sin^2 q_2 \, dq_2}{(1 + e \cos q_2)^2}.$$

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* That there is a real relationship between angular momentum and the constant h was first noticed by Nicholson some years ago (Monthly Notices of R. A. S. lxxii. p. 679 (1912)).

This can be transformed into

$$\int p_1 \, dq_1 = 16 p_2 e^2 \int_0^\infty \frac{x^2 \, dx}{(1 + x^2)(\alpha + \beta x^2)^2},$$

where
$$\alpha = 1 + e$$

and
$$\beta = 1 - e.$$

On evaluating the integral we get

$$\int p_1 \, dq_1 = 2\pi p_2 \frac{1 - (1 - e^2)^{\frac{1}{2}}}{(1 - e^2)^{\frac{1}{2}}}.$$

Now, by hypothesis (3)

$$\int p_1 \, dq_1 = \rho h,$$

and
$$2\pi p_2 = \sigma h,$$

where ρ and σ are positive integers. When these values are substituted we have

$$(\rho + \sigma)(1 - e^2)^{\frac{1}{2}} = \sigma.$$

The part which is common to all forms of the Quantum Theory can be described very simply. When systems are not exchanging energy, their equations of motion are obtained by giving a stationary value to the integral

$$\int 2L \, dt,$$

where L is the kinetic energy of the system, subject to the condition of constant energy (Principle of Least Action). The Quantum Theory lays restrictions on the interchange of energy between different systems. These restrictions require that under certain circumstances the following equation must hold

$$\int 2L \, dt = nh,$$

where h is a universal constant, n is an integer, and the integration is extended over the period of motion of the system.

Wheatstone Laboratory, King's College.
November 1915.

XXIII. *On a Comparison of the Arc and Spark Spectra of Nickel produced under Pressure. By* E. G. BILHAM [*], *B Sc., A.R.C.Sc.*

IN a recent paper †, Prof. W. G. Duffield has made a detailed comparison between the results of his investigation of the effects of increase of pressure upon the arc spectrum of nickel ‡, and those obtained by the present writer §, in which the mode of excitation was the spark between nickel electrodes connected to the secondary coil of a resonance transformer. Many interesting points of similarity are to be observed, but one's attention is immediately arrested by certain very remarkable differences.

The most noteworthy feature of the results is that, whereas the mean displacements towards the red of the lines in the spark spectrum are, upon the whole, in reasonable agreement with the means derived from the arc spectrum—assuming direct proportionality of displacement to increase of pressure, —the displacements in the arc under ten atmospheres pressure are, on the average, about twice as great as in the spark spectrum. An exception is to be observed in the case of lines which broaden slightly but symmetrically under pressure, without reversal, *i. e.*, lines of Class III. in Gale and Adams' notation. These lines appear to suffer approximately equal shifts in the two cases. For other unreversed lines the results are somewhat discordant. This is not surprising when one considers that the diffuseness of the lines under pressure renders the measurements rather uncertain even under the most favourable circumstances.

From the point of view of making a rigorous comparison between the results of the measurements of the displacements produced under the two conditions, it was somewhat unfortunate that the pressure used for my main series of experiments (namely, ten atmospheres above the normal pressure) should have happened to coincide with a region where Duffield observed an abnormally high rate of shift per atmosphere. The means at my disposal prohibited the use of pressures much higher than ten atmospheres. Apart from the fact that very radical alterations in the design of

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* Communicated by the Author.

† Phil. Mag. Sept. 1915, p. 385.

‡ Duffield, " Effect of Pressure upon Arc Spectra," No. 5, Nickel λ 3450 to λ 5500, Phil. Trans. A 215, p. 205.

§ Bilham, " The Spark Spectrum of Nickel under Moderate Pressures," Phil. Trans. A 214, p. 359.

the pressure chamber would have been necessary, the difficulty of maintaining a spark under pressure is by no means inconsiderable. The chief source of trouble lay in the rapid disintegration of the electrodes. Working with very small spark gaps, of the order of about a millimetre, a frequent result was that a short circuit was produced by a detached fragment of nickel lodging between the electrodes. Another frequent mishap was that the spark gap rapidly increased in width until a very violent discharge between projecting parts on the outside of the pressure chamber announced the fact that an easier path had been found. Clouding of the window was also a serious source of trouble. Turning to a different aspect of the case, an inspection of the appearance of the photographs produced under a pressure of eleven atmospheres points very forcibly to the conclusion that, in very many instances, measurement of the spectrum " lines " was rapidly approaching the limit of possibility on account of their diffuseness.

The above considerations will perhaps serve to show that the investigation of spark spectra under high pressures is attended with formidable difficulties, although such data would unquestionably be of great interest and value. Our knowledge of the variation of displacement with pressure in the case of spark spectra is thus limited to comparatively low pressures, and, in attempting to draw any conclusion from the published results, this must be borne in mind.

There can be no doubt, other things being equal, that the most desirable course to take in attempting to estimate the comparative magnitudes of the displacements in the arc and spark spectra, would be to compare measurements actually made under the same pressure in both cases. This procedure, as Duffield has shown, leads to the conclusion that in most cases the shifts in the arc are much higher than in the spark. The question arises as to whether such a conclusion fairly represents the case, when we consider that Duffield's measurements of the shifts in the arc at this pressure are, in general, about double the mean shifts calculated from the measurements made at pressures of from twenty to a hundred atmospheres. Although most investigators have reached the conclusion that the increase of wave length is directly proportional to the increase of pressure, there is, so far as I am aware, no reason for supposing that no departure from this law is possible in a particular instance. Moreover, the possibility exists that the relation between displacement and pressure may be different for the arc and spark spectra of the same element. Duffield has

shown, further, that the displacement does not depend solely on the applied pressure, but also on the density and temperature gradients, so that there is no *à priori* reason for expecting strict agreement between the results for arc and spark either in general or in any particular case. One must confess, however, that the discrepancies actually found are of a higher order of magnitude than might be anticipated. Further work on the spark spectrum would undoubtedly be desirable before making anything like a final decision.

Personally, I should hesitate to draw any important conclusions from the fact that my values at five atmospheres increase of pressure are relatively higher than those at ten atmospheres. The smallness of the shifts renders the order of accuracy rather low, and confers additional importance upon the personal error and upon the various causes tending to produce spurious displacements. Among these may be mentioned the effects of granularity in the plates and of lighting during the measurements. The spectrograph used for my experiments was carefully designed to eradicate, as far as possible, displacements due to changes of temperature of the grating or mounting—a fertile source of trouble in all work where the highest precision is essential. Even so, it was found impossible to completely eliminate errors due to this source, except, indeed, by increasing the number of plates for measurement. With exposures of about the same length, more uncertainty would be introduced in the cases where the displacements are smallest, that is, at the lowest pressures ; and this applies with equal force to all other sources of error. With a large grating mounted in the Rowland manner, as was employed by Duffield, the temperature effect would undoubtedly be very much larger. Without labouring the point unduly, it will be realized that we have here a cause which might easily account for the whole of the observed discrepancies between Prof. Duffield's displacements at ten atmospheres pressure and my own.

Some further light is thrown upon the question by referring to the results obtained by Humphreys and Mohler [*] at pressures of $9\frac{3}{4}$, $12\frac{1}{2}$, and $14\frac{1}{2}$ atmospheres, and by Humphreys [†] at the higher pressures of 42, 69, and 101 atmospheres. The measurements at the lower pressures are somewhat meagre, but show, on the whole, no large differences from the results obtained by taking the means of the measurements at all pressures. Thus the mean shift per atmosphere of eight lines under pressures up to $14\frac{1}{2}$ atmospheres is 2·0

* Humphreys and Mohler, Astrophysical Journal, iii. p. 114.
† Humphreys, Astrophysical Journal, xxvi. p. 36.

thousandths of an Ångström unit, compared with 1·8 from the 42 atmospheres results and 1·9 from all measurements. These lines belong to the types for which Duffield found the greatest discrepancies between the arc and spark measurements at ten atmospheres pressure—namely, those which are easily reversed. There is, in general, good agreement amongst the results of the two investigations of the arc. It seems difficult to avoid the conclusion that for some reason Duffield's measurements at ten atmospheres pressure are, on the whole, too high, and, from what has been said with regard to sources of uncertainty, the effect of temperature changes suggests itself as the most likely cause.

Comparison of Arc and Spark Displacements.

In Table I. are given the mean displacements per atmosphere in the arc found by Humphreys and Duffield respectively, and the averages of the two sets of data, for comparison with the spark displacements. Where only one set of results is available, it is given in brackets under the heading " Mean Displacement in Arc." Duffield's values at ten atmospheres and Humphreys and Mohler's low-pressure values are also given for reference. The class number for each line according to its behaviour in the spark spectrum under pressure is given in column 2.

(*Note* :—

Class I. includes lines which reverse symmetrically.

Class II.　　　,,　　,,　　,,　　,,　unsymmetrically.

Class III.　　　,,　　,,　　,,　remain bright and fairly narrow.

Class IV.　　　,,　　,,　　,,　remain bright, but are very much broadened symmetrically.

Class V.　　　,,　　,,　　,,　are very much broadened unsymmetrically towards the red.

The following classification exhibits a few alterations from that given in my original paper. After a careful re-examination of all my photographs, the lines 3510·47, 3561·91, 3624·87, 3739·38, 3783·67, and 3831·87 have been transferred from Class I. to Class II. The line 4359·76 has been transferred from Class III. to Class V.

Lines enhanced in the spark are indicated by the letter **E.**)

TABLE I.

Mean Displacements per Atmosphere in thousandths Å.U.

Wave-length λ.	Class.	Arc. Humphreys. Low Pressures.	Arc. Humphreys. All Pressures.	Arc. Duffield. 10 Atm.	Arc. Duffield. 20–100 Atm.	Mean displacement per Atm. in Arc.	Mean displacement per Atm. in Spark.
1.	2.	3.	4.	5.	6.	7.	8.
3391·21	...	1·1	1·4	...	...	(1·4)	
93·10	...	...	1·5	...	...	(1·5)	
3413·64	...	1·5	...	...	...	(1·5)	
14·96	...	1·5	1·7	...	...	(1·7)	
23·80	...	...	2·0	...	...	(2·0)	
33·71	...	...	2·3	...	...	(2·3)	
37·45	...	2·2	1·9	...	...	(1·9)	
46·34	I.	...	1·7	...	...	(1·7)	1·7
53·04	I.	...	1·5	...	...	(1·5)	1·3
54·29 E	IV.	...	...	..	...	...	1·5
58·59	I.	2·1	2·1	...	...	(2·1)	1·8
61·78	I.	1·7	1·7	...	...	(1·7)	2·5
67·63	II.	...	1·5	...	...	(1·5)	
69·64	II.	...	2·3	...	...	(2·3)	
72·68	II.	...	2·0	...	...	(2·0)	1·4
83·95	II.	...	...	...	...	...	1·5
93·10	I.	...	2·0	...	...	(2·0)	1·5
3501·00	II.	2·2	1·8	...	(1·5)	1·7	1·5
10·47	II.	...	2·0	...	2·6	2·3	2·2
15·17	I.	2·8	2·5	...	...	(2·5)	2·7
19·90	II.	...	1·8	...	1·4	1·6	1·9
24·65	I.	2·4	2·3	...	...	(2·3)	3·0
28·10	II.	...	...	...	...	...	1·8
48·34	II.	...	2·0	...	1·2	1·6	2·1
61·91	II.	...	1·5	...	0·7	1·1	1·1
66·50	I.	...	2·2	...	2·1	2·1	2·0
71·99	II.	...	2·4	...	1·9	2·1	1·8
76·91 E	IV.	...	...	...	...	...	8·2
88·08	II.	...	2·2	...	1·1	1·6	1·4
3597·84	II.	...	2·4	4·9	2·1	2·2	2·1
3602·41	II.	...	2·0	3·1	1·8	1·9	1·6
09·44	I.	...	1·8	2·9	1·0	1·4	1·6
10·60	II.	...	2·4	6·4	2·2	2·3	2·6
12·86	II.	...	2·0	4·4	1·4	1·7	1·6
19·52	I.	...	1·6	4·7	2·6	2·1	1·8
24·87	II.	...	1·5	3·4	0·8	1·1	0·7
35·07	III.	...	...	4·7	1·5	(1·5)	5·1
62·10	III.	...	1·3	3·7	1·1	1·2	3·5
64·24	II.	...	1·6	4·8	1·7	1·7	2·2
69·39	II.	...	...	3·1	1·3	(1·3)	1·2
70·57	II.	...	1·3	3·9	2·1	1·8	2·5
74·26	II.	...	1·0	4·2	1·7	1·4	1·9
88·58	II.	...	1·0	3·7	1·8	1·4	2·0
94·07	III.	...	...	2·6	1·3	(1·3)	2·5

Wave-length A.	Class.	Arc.				Mean displacement. per Atm. in Arc.	Mean displacement. per Atm. in Spark.
		Humphreys.		Duffield.			
		Low Pressures.	All Pressures.	10 Atm.	20–100 Atm.		
1.	2.	3.	4.	5.	6.	7.	8.
3722·63	II.	...	1·6	...	2·2	1·9	2·9
36·94	II.	...	1·2	...	1·6	1·4	1·0
39·38	II.	...	...	...	1·2	(1·2)	1·0
69·62 E	IV.	...	...	4·0	1·4	(1·4)	7·7
75·71	II.	...	1·3	1·0	1·5	1·4	2·2
83·67	II.	...	0·9	1·3	1·3	1·1	1·6
3807·30	II.	...	1·1	3·0	1·5	1·3	1·8
31·87	II.	...	...	3·2	1·8	(1·8)	3·6
49·70 E	IV.	...	...	..	...	...	14·9
58·40	I.	...	1·7	3·9	2·1	1·9	2·1
3972·31	III.	...	1·1	1·2	0·8	1·0	2·8
73·70	V.	...	2·0	4·4	1·9	2·0	5·8
4121·48	III.	...	...	3·9	1·7	(1·7)	2·6
42·47	III.	...	...	10·5	...	...	3·2
4288 20	V.	...	...	16·2	10·9	(10·9)	12·1
4330·85 } 31·78 }	III.	...	2·1	6·3	3·0	2·6	4·4
59·76	V.	...	...	11·5	12·2	(12·2)	10·6
4401·70	V.	...	4·8	11·6	12·0	8·4	10·2
4459·25	V.	...	6·2	10·2	10·9	8·6	9·3
62·65	V.	...	...	12·3	9·5	(9·5)	9·9
70·61	V.	...	8·5	12·4	11·0	9·7	8·9
4520·20	...	...	1·8	3·1	1·7	1·8	
92·69	V.	...	8·5	14·1	10·3	9·4	11·8
4600·51	IV.	...	11·3	13·8	9·3	10·3	
05·15	V.	...	7·8	12·0	9·5	8·7	
48·82	V.	...	8·1	14·0	11·4	9·8	
86·39	III.	...	8·0	18·4	11·7	9·4	
4714·59	V.	...	6·7	17·1	11·1	8·9	
56·70	V.	...	7·2	15·7	11·3	9·3	

The mean shifts for the lines in each class have been computed for comparison with the values found by Duffield for the arc. Only lines figuring in both investigations have been included.

TABLE II.

Class.	Number of Lines.	Mean displacement per Atmosphere.		Ratio Spark : Arc.
		Arc (Duffield).	Spark.	
I.	4	1·95	1·88	0·96
II.	24	1·60	1·85	1·16
III.	6	1·57	3·48	2·22
IV.	1	1·4	7·7	5·50
V.	8	9·84	9·83	1·00

If Humphreys' data are included in obtaining the means for the arc, the results are only slightly modified as in Table III.

TABLE III.

Class.	Number of Lines.	Mean Displacement per Atmosphere.		Ratio Spark : Arc.
		Arc (Humphreys and Duffield).	Spark.	
I.	11	1·94	2·00	1·03
II.	25	1·64	1·84	1·12
III.	6	1·55	3·48	2·25
IV.	1	1·4	7·7	5·50
V.	8	8·84	9·83	1·11

From an inspection of Tables II. and III. we arrive at the interesting conclusion that the arc and spark shifts are, on the whole, very nearly equal for lines in Classes I., II., and V., but for lines in Class III. the spark displacement is rather more than twice that in the arc. The values for Class IV. rest upon the results for a single line, so that the probability of error is too great to permit of any important conclusions being drawn. It is a significant fact that certain lines in Class V. show signs of reversal in the spark under a pressure of eleven atmospheres. For example, the reversal of the line 4401·77, a typical specimen of this class, can be distinctly seen in Plate i. of my original paper. In the arc this line is given by Duffield as suffering immense unsymmetrical broadening, without reversal even at the highest pressures. If we regard the continuous spectrum, which is so prominent in the more refrangible region of the spark spectrum, as being due to immense broadenings of lines of Classes I. and II. it is evident that Class V. lines have something in common with those of Classes I. and II., although at first sight nothing could appear more dissimilar.

The view I have taken—namely, that Duffield's displacements at ten atmospheres pressure are uniformly too high—thus leads us to the conclusion that the behaviour of lines easily reversed, or tending to reverse, is approximately the same whether developed in the arc or spark under pressure.

Abnormalities or discrepancies are exhibited by unreversed
lines. It will be observed that this result is exactly the
opposite of that reached by Duffield's analysis of the data,
and supported by the theory he gives concerning the part
played by the density and temperature gradients. It remains
for further investigation to decide whether this view is
correct. The whole question turns very largely upon the
reality of an abnormally large rate of displacement with
pressure in the nickel arc at relatively low pressures ; and
confirmation of Prof. Duffield's conclusion may be regarded
as one of the most pressing problems in this branch of
spectroscopy.

The part played by the temperature and density gradients
in determining the position of the maximum of emission or
absorption in a spectrum line is a problem which is becoming
increasingly more prominent with every fresh advance in
this line of investigation. It must be confessed that we are
still far from a complete interpretation of all the manifold
phenomena which present themselves. All that we can
really be sure about at present is that the measured displace-
ment is made up of a component directly due to the increase
of pressure and probably proportional to it, together with a
component of uncertain magnitude which has its origin in
the changes in the structure of the line due to the alterations
of the conditions prevailing in the source of emission. To
what extent it may be possible eventually to disentangle the
two components one cannot at present say. Meanwhile, as
Dr. Royds * has recently remarked, the most valuable
method of attack appears to be that of the electric furnace,
in which the vapour density is likely to be influenced by
pressure to a much less extent than in the arc or spark. In
any case, the recognition of the existence of these phenomena
is of the first importance, not only in interpreting existing
results, but also in determining the most profitable directions
for future research.

Kew Observatory,
  November 1915.

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* Kodaikanal Observatory Bulletin, No. xliii.

XXIV. *A Notation for Zeeman Patterns.*
By W. M. Hicks, *F.R.S.*[*]

THE convenience of a generally recognized and concise notation to represent the configuration of the components when a spectral line is decomposed in a magnetic field is evident. I have found the following very useful for entering on handlists of spectral lines, and offer it as a suggestion for general use. Runge has shown that the displacements of the various components in a given field are multiples or submultiples of a constant unit. The wavenumber displacement chosen by him as the unit is that of what is commonly called the normal triplet—the theoretical value for an electron revolving round a centre of attraction. It is convenient to take one third of this, in order to avoid the frequent appearance of fractions. Using the very careful determination from Cd and Zn by Fräulein Stellenheimer [†] working in Prof. Paschen's laboratory, this constant is given by $10^{-5}d\lambda/\lambda^2H = 1.584$. As the displacements take place in general symmetr cally on both sides of the undisplaced line, it is only necessary to tabulate those on each side and to indicate the distances as multiples of the unit. From analogy with the usual diagrammatic method of indicating a Zeeman pattern, the displacement of lines vibrating parallel to the field may be written as a numerator, whilst those perpendicular are indicated in the denominator. Thus the normal triplet would be written $\frac{0}{3}$ or printed 0 | 3. In cases where it is desirable to indicate relative intensities subscript figures may be attached, or—for printed matter where such subscripts are inconvenient—by figures in brackets, as is done below.

With this notation the patterns for the various kinds of series are then represented as follows:—

Doublets.

$S_1, P_1.$		$S_2, P_2.$
2 | 6.10,		4 | 8.

$D_{12}.$	$D_{11}.$	$D_{21}.$
5 | 10,	0 | $6\frac{1}{2}$,	0 | 5.

The satellite pattern (D_{12}) does not seem to be the same

for all metals. Thus for Tl D_{12} it is 5 | $3\frac{1}{2}$.6.10, for Ca and
Sr 5 | 6, for Ba 5 | 3.6.10; and it would appear that the
typical form is 5 | 3.6.10, but that some of the perpendicular
vibrations (3.6.10) may be too faint to be observed. In
Mg—which does not exhibit satellites—the line keeps to
the D_{11} type. In others— *e. g.* in the Cu line 5700—the pattern
is 5 | 3.6$\frac{1}{2}$.10. It belongs to a doublet of the D type which
shows no satellites, and the pattern seems to be that of a
combined D_{11} and D_{12}. The corresponding doublets in Ag
and Au show satellites, and in these each component exhibits
the normal pattern for each.

Triplets.

S_1.	S_2.	S_3
0.3	6.9.12,	3	9.12,	0	12.

The remark above as to the absence of a component being
apparent only is well illustrated by the case of HgS_1 and HgS_2.
Thus indicating intensities by numbers in brackets after the
figure giving the displacement, we have for the first three
triplets:—

$S_1(1)$.	$S_1(2)$.	$S_1(3)$.
0(4).3(3)	6(4).9(5).12(3),	0(2).3(1)	6(2).9(1).12(3),	0(1)	6(1).

$S_2(1)$.	$S_2(2)$.	$S_2(3)$.
3(4)	9(4).12(5),	3(1)	9(2).12(2),	?	9.

Judging from the rate of decay of intensity with in-
creasing order, however, we might have expected the com-
ponent 12 to be the last to go in $S_1(3)$.

D_{13}.	D_{12}.	D_{11}.	D_{22}.	D_{21}.	D_{31}.
?	4	7,	0	7,	?	0	6,	0	3.

The satellite patterns, as in the case of the doublet series,
are not uniform. Thus for D_{13}, Ca has 0 | $6\frac{1}{2}$, Sr 0 | 15,
Cd 4 | 10, Hg 0.6 | 3.9.15. It is interesting to note that
the abnormality for Sr and Cd is shown also in their deviation
from the rule that the mantissæ of the denominators of $D_{13}(2)$
are multiples of Δ_2—in these elements the multiple occurring
in D_{12} and D_{11} instead*. For D_{22} the normal type is
probably 6 | 3.9 Ca and Zn give 6 | 6, Sr 0 | 9, Cd and
Hg 6 | 3.9. Hg D(2) has very complicated and abnormal
patterns, and as is known the satellites themselves have

* Phil. Trans. A. ccxiii. p. 374 (1913).

separations quite out of step with the typical values. The measurements of Runge and Paschen for Hg D(2) give

$$D_{13}. \qquad\qquad D_{12}. \qquad\qquad D_{11}.$$
$$0.6 \mid 3.9.15, \quad 2.4\tfrac{1}{2}.7\tfrac{1}{2} \mid 4.6\tfrac{1}{2}.9.11, \quad 2 \mid 7 \text{ instead of } 0 \mid 7,$$

$$D_{22}. \qquad\qquad D_{21}. \qquad\qquad D_{31}.$$
$$6 \mid 3.9.12, \qquad\quad 0.2 \mid 5.7, \qquad\quad 0.3 \mid 3.$$

For Hg D(3) the strong lines appear normal, whilst that for Hg $D_{11}(4)$ is $0 \mid 6$—possibly observation error for $0 \mid 7$, as the components are very faint.

The University, Sheffield.

XXV. *Intelligence and Miscellaneous Articles.*

HENRY GWYN JEFFREYS MOSELEY.

THE brilliant young physicist who was killed in action on August 10th at the Dardanelles was the only son of my close friend and fellow student the late Professor Henry Nottidge Moseley, F.R.S., of Oxford. He was educated at Eton, where he entered as a scholar, and at Trinity College, Oxford, where he gained a Millard scholarship. He obtained a First Class in Mathematical Moderations and Honours in Natural Science.

Harry Moseley was a most loveable boy and early showed great enthusiasm for science and marked originality. On leaving Oxford in 1910, he was appointed by Professor Rutherford of Manchester as lecturer and demonstrator in the Physics department of the University. After two years he resigned his lectureship and was awarded the John Harling Fellowship, which enabled him to devote his energies entirely to research. In 1913 he returned to Oxford to live with his mother, and continued his experiments in the laboratory of Professor Townsend. He went in the summer of 1914 to the meeting of the British Association in Australia; but on the outbreak of war made as speedily as possible for England, and resigning all thought of continuing the researches in which he was so successfully engaged, applied for and obtained a Commission in the Royal Engineers. He was, I am assured, offered work suited to his scientific capacities at home, but deliberately chose to share with others of his age the dangers of active service. He was made signalling officer to the 38th Brigade of the First Army, and left for the Dardanelles on June 13th, 1915. There, in the beginning of August, he was instantaneously killed by a bullet through the head as he was in the act of telephoning an order to his division. He was only 27 years of age.

Sir Ernest Rutherford writes that Moseley was " one of those rare examples of a man who was a born investigator." This quality he inherited from his father ; and it is noteworthy that his grandfather Canon Moseley, F.R.S., was a distinguished and original mathematical physicist, whilst his grandfather on his mother's side, Mr. Gwyn Jeffreys, was also a Fellow of the Royal Society and for many years a leader in the study of Oceanography and Marine Zoology.   Professor Rutherford tells us that Harry Moseley's " undoubted originality and marked capacity as an investigator were very soon ungrudgingly recognized by his co-workers in the laboratory, while his cheerfulness and willingness to help in all possible ways endeared him to all his colleagues." Mr. C. G. Darwin, a grandson of Charles Darwin—who worked with him at Manchester and produced with him a joint paper in which they mapped out accurately, for the first time, the spectrum of the characteristic X-radiation from an X-ray tube with a platinum anticathode,— writes that he was without exception or exaggeration the most brilliant man whom he had ever come across.   Others who came to know him well in Manchester write of his charm of manner and personality, of his kindliness and unselfishness and care for the interests of others.   As a boy (when I knew him best) he was a keen and observant naturalist and knew every bird and bird's nest in the neighbourhood of his home.   In this and in the collection of flint implements he was enthusiastically aided by his sister.   His last letters home from the East were full of observations on the plant-life, the birds, the beasts, and the flint implements *of all ages* which he found in a day's ramble on the hills where he was encamped.   A most happy life of experimental research, with natural history and his garden as relaxations, was assured to one so greatly gifted and beloved, for he had private means and an ideal home.   Whilst abroad on active service, in view of possibilities now alas! realized, Harry Moseley expressed the wish (which will be eventually carried out) to bequeath any property at his disposal to the Royal Society of London " for the furtherance of scientific research."

I am enabled by the kindness of Dr. Bohr of the University of Manchester, who has been aided by Dr. Makower, to add to this short personal sketch a notice of Moseley's scientific work which will, I am sure, be highly valued by the readers of the Phil. Mag.

E. RAY LANKESTER, Dec. 24, 1915.

MOSELEY came to Manchester in the spring of 1910 as lecturer and demonstrator in the Physical Laboratories of the University. At that time a great number of scientists from all parts of the world were working in the laboratories under the direction and inspiration of Sir Ernest Rutherford.   Moseley at once caught the spirit of the laboratories and applied himself with characteristic energy and enthusiasm to the difficult and important problem of determining the number of β-particles emitted by a

radioactive atom on disintegration. This problem had been investigated only for the active deposit of radium, and even in this case no high degree of accuracy could be claimed for the result of previous investigators. Moseley succeeded in improving the method and in obtaining much more accurate results. He also extended the investigation so as to include most of the radioactive products emitting β-rays *. His results have since gained additional importance on account of their bearing on theories of the origin of β- and γ-rays. The knowledge and experience which he gained in these experiments Moseley subsequently used to obtain high potentials in vacuo by means of the charge acquired by a radioactive substance during the emission of β-rays †. He was thus able to obtain higher steady potentials than had previously been reached in this or any other way. Whilst engaged in these difficult researches Moseley still found time to devote attention to other problems. In collaboration with Fajans he developed a most interesting method of determining the life of very rapidly decaying radioactive products ‡; with Makower he discovered that radium B emitted γ-rays which were so easily absorbed that they had not been previously detected §; and with Robinson he measured the total ionization produced by the β and γ radiation from radium B and radium C ‖.

In 1912 Moseley resigned his lectureship, and having obtained the John Harling Fellowship at Manchester University, he was able to devote all his time to scientific investigation. In the same year a new field of Physical research was created by Laue's discovery of the interference of X-rays in crystals; and interest was soon intensified by the brilliant work of W. H. and W. L. Bragg on the constitution of X-rays and the structure of crystals. Very soon after Laue's discovery Moseley, working with Darwin, started a thorough investigation of the properties of X-rays by means of the new method. Their results were published in June 1913 ¶; and although many of the results were discovered and published earlier by the Braggs, this paper contained a great number of most interesting experimental details and theoretical considerations, and constituted an important step in the rapidly increasing knowledge about the nature of X-rays. Immediately after the completion of this work Moseley undertook a systematic investigation of the characteristic X-radiation from as many different elements as possible. This investigation involved great experimental difficulties, partly on account of the fact that the chemical nature of many

* Moseley, Proc. Roy. Soc. A. lxxxvii. p. 230 (1912).
† Moseley, Proc. Roy. Soc. A. lxxxviii. p. 471 (1913).
‡ Moseley and Fajans, Phil. Mag. xxii. p. 629 (1911).
§ Moseley and Makower, Phil. Mag. xxiii. p. 312 (1912).
‖ Moseley and Robinson, Phil. Mag. xxviii. p. 327 (1914).
¶ Moseley and Darwin, Phil. Mag. xxvi. p. 210 (1913).

elements makes them rather unsuitable as anticathodes in X-ray tubes, and partly on account of the extreme absorbability of the radiation from many of the elements. Nevertheless, by his wonderful energy and by an ingeniously simple experimental arrangement for photographing the X-ray spectra, Moseley in less than half a year obtained measurements of the wave-lengths of the most intense lines in the high-frequency spectra of the greater part of the known elements and discovered the fundamental laws, which will always bear his name*. This work, begun in Manchester, was completed in Oxford in the early spring of 1914. As is well known, Moseley found that the frequencies of the principal lines in the high-frequency spectra are simple functions of the whole number which represents the position of the elements in the periodic table of Mendelejeff. The extreme importance of this result is that it reveals a relation between properties of different elements far simpler than any which could be expected from properties previously investigated, all of which, including the ordinary visible spectra, vary in an intricate manner from element to element. Moseley's discovery therefore gives a most important clue to the question of the internal structure of the atom which has received so much attention in recent years. While it is hardly the place here to enter into this problem in any detail, the general importance of Moseley's results is perhaps best illustrated by the fact that they enabled him to predict with certainty the number of possible elements hitherto unknown and their position in the periodic series. In this way he was, for instance, able to fix the number of possible elements in the group of the rare earths ; and just before he went to Australia he was occupied in collaboration with Prof. Urbain on an investigation of the high-frequency spectra of the elements of this group, which no doubt will throw very much light upon this field of investigation which hitherto has given chemists so much trouble. A full account of this investigation has not yet been published, but Moseley gave a paper on the general question before the Meeting of the British Association in Sydney.

Every reader of Moseley's papers will be strongly impressed by his penetrating theoretical understanding and his great experimental skill which, together with his unique capacity for work, have secured him a place among the foremost workers in science of his time, although he was not able to devote more than four short years to scientific investigations.

* Moseley, Phil. Mag. xxvi. p. 1024 (1913), and xxvii. p. 703 (1914).

XXVI. *On the Electrical Capacity of Approximate Spheres and Cylinders.* By Lord RAYLEIGH, *O.M., F.R.S.*[*]

MANY years ago I had occasion to calculate these capacities [†] so far as to include the squares of small quantities, but only the results were recorded. Recently, in endeavouring to extend them, I had a little difficulty in retracing the steps, especially in the case of the cylinder. The present communication gives the argument from the beginning. It may be well to remark at the outset that there is an important difference between the two cases. The capacity of a sphere situated in the open is finite, being equal to the radius. But when we come to the cylinder, supposed to be entirely isolated, we have to recognise that the capacity reckoned per unit length is infinitely small. If a be the radius of the cylinder and b that of a coaxal enveloping case at potential zero, the capacity of a length l is [‡]

$$\frac{\frac{1}{2}l}{\log (b/a)},$$

which diminishes without limit as b is increased. For clearness it may be well to retain the enveloping case in the first instance.

In the intervening space we may take for the potential in terms of the usual polar coordinates

$$\phi = H_0 \log (r/b) + H_1 r^{-1} \cos (\theta - \epsilon_1) + K_1 r \cos (\theta - \epsilon_1') + \ldots$$
$$+ H_n r^{-n} \cos (n\theta - \epsilon_n) + K_n r^n \cos (n\theta - \epsilon_n').$$

Since $\phi = 0$ when $r = b$,

$$\epsilon_n' = \epsilon_n, \quad K_n = -H_n b^{-2n},$$

and

$$\phi = H_0 \log (r/b) + H_1 \left(\frac{1}{r} - \frac{r}{b^2} \right) \cos (\theta - \epsilon_1)$$
$$+ H_2 \left(\frac{1}{r^2} - \frac{r^2}{b^4} \right) \cos (2\theta - \epsilon_2) + \ldots \quad \ldots \quad (1)$$

At this stage we may suppose b infinite in connexion with H_1, H_2, &c., so that the positive powers of r disappear. For brevity we write $\cos (n\theta - \epsilon_n) = F_n$, and we replace r^{-1} by u. Thus

$$\phi = -H_0 \log (ub) + H_1 u F_1 + H_2 u^2 F_2 + \ldots \quad \ldots \quad (2)$$

We have now to make $\phi = \phi_1$ at the surface of the approximate cylinder, where ϕ_1 is constant and

$$u = u_0 + \delta u = u_0 (1 + C_1 G_1 + C_2 G_2 + \ldots).$$

Herein

$$G_n = \cos (n\theta - e_n),$$

and the C's are small constants. So far as has been proved, e_n might differ from ϵ_n, but the approximate identity may be anticipated, and at any rate we may assume for trial that it exists and consider G_n to be the same as F_n, making

$$u = u_0 + \delta u = u_0 (1 + C_1 F_1 + C_2 F_2 + \ldots). \quad \ldots \quad (3)$$

On the cylinder we have

$$\phi_1 = -H_0 \log (u_0 b) + H_1 u_0 F_1 + H_2 u_0^2 F_2 + \ldots$$
$$+ \frac{\delta u}{u_0} \left\{ -H_0 + H_1 u_0 F_1 + 2H_2 u_0^2 F_2 + 3H_3 u_0^3 F_3 + \ldots \right\}$$
$$+ \left(\frac{\delta u}{u_0} \right)^2 \left\{ \tfrac{1}{2} H_0 + H_2 u_0^2 F_2 + 3H_3 u_0^3 F_3 + \ldots \right.$$
$$\left. + \tfrac{1}{2} p(p-1) H_p u_0^p F_p \right\}, \quad \ldots \quad (4)$$

and in this

$$\delta u / u_0 = C_1 F_1 + C_2 F_2 + C_3 F_3 + \ldots \quad \ldots \quad (5)$$

The electric charge Q, reckoned per unit length of the cylinder, is readily found from (2). We have, integrating round an enveloping cylinder of radius r,

$$Q = -\frac{1}{4\pi}\int_0^\pi \frac{d\phi}{dr} r \, d\theta = -\frac{H_0}{2}, \quad . \quad . \quad . \quad . \quad (6)$$

and Q/ϕ_1 is the *capacity*.

We now introduce the value of $\delta u/u_0$ from (5) into (4) and make successive approximations. The value of H_n is found by multiplication of (4) by F_n, where $n = 1, 2, 3$, &c., and integration with respect to θ between 0 and 2π, when products such as $F_1 F_2$, $F_2 F_3$, &c., disappear. For the first step, where C^2 is neglected, we have

$$0 = H_n u_0{}^n \int F_n{}^2 d\theta - H_0 C_n \int F_n{}^2 d\theta, \quad . \quad . \quad . \quad . \quad (7)$$

or

$$H_n u_0{}^n = H_0 C_n. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Direct integration of (4) gives also

$$\phi_1 = -H_0 \log (u_0 b) + \int \frac{d\theta}{2\pi} \frac{\delta u}{u_0} \{ H_1 u_0 F_1 + 2 H_2 u_0{}^2 F_2$$

$$+ 3 H_3 u_0{}^3 F_3 + \ldots \} + \tfrac{1}{2} H_0 \int \frac{d\theta}{2\pi} \left(\frac{\delta u}{u_0}\right)^2, \quad . \quad . \quad . \quad (9)$$

cubes of C being neglected at this stage. On introduction of the value of H_n from (8) and of δu from (5),

$$\phi_1 = -H_0 \log (u_0 b) + \tfrac{1}{4} H_0 \{ 3 C_1{}^2 + 5 C_2{}^2 + 7 C_3{}^2 + \ldots \}. \quad (10)$$

Thus

$$\phi_1/Q = 2 \log (u_0 b) - \tfrac{1}{2} \{ 3 C_1{}^2 + 5 C_2{}^2 + 7 C_3{}^2 + \ldots \} \quad . \quad . \quad (11)$$

In the application to an electrified liquid considered in my former paper, it must be remembered that u_0 is not constant during the deformation. If the liquid is incompressible, it is the volume, or in the present case the sectional area (σ), which remains constant. Now

$$2\sigma = \int_0^{2\pi} \frac{d\theta}{(u_0 + \delta u)^2} = \frac{1}{u_0{}^2} \int d\theta \left\{ 1 - 2 \frac{\delta u}{u_0} + 3 \left(\frac{\delta u}{u_0}\right)^2 \right\}$$

$$= \frac{2\pi}{u_0{}^2} \{ 1 + \tfrac{3}{2} (C_1{}^2 + C_2{}^2 + C_3{}^2 + \ldots) \},$$

so that if a denote the radius of the circle whose area is σ,

$$u_0{}^2 = a^{-2} \{ 1 + \tfrac{3}{2} (C_1{}^2 + C_2{}^2 + C_3{}^2 + \ldots) \}. \quad . \quad . \quad (12)$$

Accordingly,

$$\log u_0^2 = -2 \log a + \tfrac{3}{2}(C_1^2 + C_2^2 + C_3^2 + \ldots),$$

and (11) becomes

$$\phi_1/Q = 2 \log (b/a) - C_2^2 - 2C_3^2 - \ldots - (p-1)C_p^2, \quad . \quad (13)$$

the term in C_1 disappearing, as was to be expected.

The potential energy of the charge is $\tfrac{1}{2}\phi_1 Q^2$. If the change of potential energy due to the deformation be called P', we have

$$P' = -\tfrac{1}{2}Q^2\{C_2^2 + 2C_3^2 + \ldots + (p-1)C_p^2\}, \quad . \quad (14)$$

in agreement with my former results.

There are so few forms of surface for which the electric capacity can be calculated that it seems worth while to pursue the approximation beyond that attained in (11), supposing, however, that all the ϵ's vanish, everything being symmetrical about the line $\theta = 0$. Thus from (4), as an extension of (7) with inclusion of C^2,

$$0 = (H_n u_0^n - H_0 C_n)\int \frac{d\theta}{2\pi} F_n^2$$
$$+ \int \frac{d\theta}{2\pi} F_n(C_1 F_1 + C_2 F_2 + \ldots)(H_1 u_0 F_1 + 2H_2 u_0^2 F_2$$
$$+ 3H_3 u_0^3 F_3 + \ldots)$$
$$+ \frac{H_0}{2}\int \frac{d\theta}{2\pi} F_n(C_1 F_1 + C_2 F_2 + C_3 F_3 + \ldots)^2, \quad . \quad . \quad . \quad (15)$$

or with use of (8)

$$u_0^n H_n/H_0 = C_n - \int_0^{2\pi} \frac{d\theta}{2\pi} F_n(C_1 F_1 + C_2 F_2 + C_3 F_3 + \ldots)$$
$$(3C_1 F_1 + 5C_2 F_2 + 7C_3 F_3 + \ldots), \quad . \quad (16)$$

by which H_n is determined by means of definite integrals of the form

$$\int_0^{2\pi} F_n F_p F_q \, d\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

n, p, q being positive integers. It will be convenient to donote the integral on the right of (16) by I_n, I_n being of the second order in the C's.

Again, by direct integration of (4) with retention of C^3,

$$\phi_1 = -H_0 \log(u_0 b) + \int \frac{d\theta}{2\pi} (C_1 F_1 + C_2 F_2 + C_3 F_3 + \ldots)$$
$$(H_1 u_0 F_1 + 2H_2 u_0^2 F_2 + 3H_3 u_0^3 F_3 + \ldots)$$
$$+ \tfrac{1}{2} H_0 \int \frac{d\theta}{2\pi} (C_1 F_1 + C_2 F_2 + C_3 F_3 + \ldots)^2$$
$$+ \int \frac{d\theta}{2\pi} (C_1 F_1 + C_2 F_2 + C_3 F_3 + \ldots)^2 (H_2 u_0^2 F_2 + 3H_3 u_0^3 F_3$$
$$+ \ldots + \tfrac{1}{2} p(p-1) H_p u_0^p F_p).$$

In the last integral we may substitute the first approximate value of H_p from (8). Thus in extension of (11)

$$\phi_1/Q = 2\log(u_0 b) - \tfrac{1}{2}\{3C_1^2 + 5C_2^2 + 7C_3^2 + \ldots\}$$
$$+ C_1 I_1 + 2C_2 I_2 + 3C_3 I_3 + \ldots$$
$$- \int_0^{2\pi} \frac{d\theta}{\pi} (C_1 F_1 + C_2 F_2 + C_3 F_3 + \ldots)^2 \{C_2 F_2 + 3C_3 F_3 + \ldots$$
$$+ \tfrac{1}{2} p(p-1) C_p F_p\} \quad . \quad . \quad . \quad (18)$$

The additional integrals required in (18) are of the same form (17) as those needed for I_n.

As regards the integral (17), it may be written

$$\int_0^{2\pi} d\theta \cos n\theta \cos p\theta \cos q\theta.$$

Now four times the latter integral is equal to the sum of integrals of cosines of $(n-p-q)\theta$, $(n-p+q)\theta$, $(n+p-q)\theta$, and $(n+p+q)\theta$, of which the last vanishes in all cases. We infer that (17) vanishes unless one of the three quantities n, p, q is equal to the sum of the other two. In the excepted cases

$$(17) = \tfrac{1}{2}\pi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

If p and q are equal, (17) vanishes unless $n=2p$; also whenever n, p, q are all odd.

We may consider especially the case in which only C_p occurs, so that

$$u = u_0(1 + C_p \cos p\theta) \quad . \quad . \quad . \quad . \quad . \quad (20)$$

In (16)

$$I_n = (2p+1)C_p^2 \int_0^{2\pi} \frac{d\theta}{2\pi} F_n F_p^2,$$

so that I_n vanishes unless $n=2p$. But I_{2p} disappears in (18), presenting itself only in association with C_{2p}, which

we are supposing not to occur. Also the last integral in (18) makes no contribution, reducing to

$$\tfrac{1}{2}p(p-1)\mathrm{C}_p{}^3 \int_0^{2\pi} \frac{d\theta}{\pi} \cos^3 p\theta,$$

which vanishes. Thus

$$\phi_1/\mathrm{Q} = 2 \log{(u_0 b)} - (p+\tfrac{1}{2})\mathrm{C}_p{}^2, \quad . \quad . \quad . \quad (21)$$

the same as in the former approximation, as indeed might have been anticipated, since a change in the sign of C_p amounts only to a shift in the direction from which θ is measured.

The corresponding problem for the approximate sphere, to which we now proceed, is simpler in some respects, though not in others. In the general case u, or r^{-1}, is a function of the two angular polar coordinates θ, ω, and the expansion of δu is in Laplace's functions. When there is symmetry about the axis, ω disappears and the expansion involves merely the Legendre functions $\mathrm{P}_n(\mu)$, in which $\mu = \cos\theta$. Then

$$u = u_0 + \delta u = u_0 \{1 + \mathrm{C}_1\mathrm{P}_1(\mu) + \mathrm{C}_2\mathrm{P}_2(\mu) + \ldots\}, \quad . \quad . \quad (22)$$

where $\mathrm{C}_1, \mathrm{C}_2, \ldots$ are to be regarded as small. We will assume δu to be of this form, though the restriction to symmetry makes no practical difference in the solution so far as the second order of small quantities.

For the form of the potential (ϕ) outside the surface, we have

$$\phi = \mathrm{H}_0 u + \mathrm{H}_1 u^2 \mathrm{P}_1(\mu) + \mathrm{H}_2 u^3 \mathrm{P}_2(\mu) + \ldots; \quad . \quad . \quad . \quad (23)$$

and on the surface

$$\phi_1 = \mathrm{H}_0 u_0 + \mathrm{H}_1 u_0{}^2 \mathrm{P}_1 + \mathrm{H}_2 u_0{}^3 \mathrm{P}_2 + \ldots$$
$$+ \delta u \{\mathrm{H}_0 + 2u_0 \mathrm{H}_1 \mathrm{P}_1 + 3u_0{}^2 \mathrm{H}_2 \mathrm{P}_2 + \ldots\}$$
$$+ (\delta u)^2 \{\mathrm{H}_1 \mathrm{P}_1 + 3u_0 \mathrm{H}_2 \mathrm{P}_2 + \ldots + \tfrac{1}{2}p(p+1)u_0{}^{p-1}\mathrm{H}_p \mathrm{P}_p\}, \quad (24)$$

in which we are to substitute the values of δu, $(\delta u)^2$ from (22). In this equation ϕ_1 is constant, and $\mathrm{H}_1, \mathrm{H}_2, \ldots$ are small in comparison with H_0.

The procedure corresponds closely with that already adopted for the cylinder. We multiply (24) by P_n, where n is a positive integer, and integrate with respect to μ over angular space, *i. e.* between -1 and $+1$. Thus, omitting the terms of the second order, we get

$$u_0{}^n \mathrm{H}_n = -\mathrm{H}_0 \mathrm{C}_n \quad . \quad . \quad . \quad . \quad . \quad (25)$$

as a first approximation to the value of H_n.

Direct integration of (24) gives

$$\phi_1 \int d\mu = H_0 u_0 \int d\mu + u_0 \int \{C_1 P_1 + C_2 P_2 + \ldots\}$$
$$\{2u_0 H_1 P_1 + 3u_0^2 H_2 P_2 + \ldots\} d\mu$$
$$= H_0 u_0 \int d\mu + u_0 \int \{2u_0 H_1 C_1 P_1^2 + 3u_0^2 H_2 C_2 P_2^2$$
$$+ 4u_0^3 H_3 C_3 P_3^2 + \ldots\} d\mu,$$

or on substitution for H_n from (25)

$$\phi_1 = H_0 u_0 \left\{ 1 - \tfrac{2}{3} C_1^2 - \tfrac{3}{5} C_2^2 - \ldots - \frac{p+1}{2p+1} C_p^2 \right\}, \quad . \quad . \quad (26)$$

inasmuch as

$$\int_{-1}^{+1} P_p^2(\mu)\, d\mu = \frac{2}{2p+1} \quad . \quad . \quad . \quad . \quad (27)$$

As appears from (23), H_0 is identical with the electric charge upon the sphere, which we may denote by Q, and Q/ϕ_1 is the electrostatic capacity, so that to this order of approximation

$$\text{Capacity} = u_0^{-1} \left\{ 1 + \tfrac{2}{3} C_1^2 + \ldots + \frac{p+1}{2p+1} C_p^2 \right\} \quad . \quad . \quad (28)$$

Here, again, we must remember that u_0^{-1} differs from the radius of the true sphere whose volume is equal to that of the approximate sphere under consideration. If that radius be called a

$$u_0^{-1} = a \left\{ 1 - \frac{2C_1^2}{3} - \frac{2C_2^2}{5} - \ldots - \frac{2C_p^2}{2p+1} \right\}, \quad . \quad . \quad (29)$$

and

$$\text{Capacity} = a \left\{ 1 + \frac{C_2^2}{5} + \ldots + \frac{n-1}{2n+1} C_n^2 \right\}, \quad . \quad . \quad (30)$$

in which C_1 does not appear.

The potential energy of the charge is $\tfrac{1}{2} Q^2 \div \text{Capacity}$. Reckoned from the initial configuration $(C=0)$, it is

$$P' = -\frac{Q^2}{2a} \left\{ \frac{C_2^2}{5} + \ldots + \frac{p-1}{2p+1} C_p^2 \right\} \quad . \quad . \quad (31)$$

It has already been remarked that to this order of approximation the restriction to symmetry makes little

difference. If we take

$$\delta u/u_0 = F_1 + F_2 + \ldots + F_n, \quad . \quad . \quad . \quad . \quad (32)$$

where the F's are Laplace's functions,

$$\frac{1}{4\pi} \iint F_p^2 \, d\mu \, d\omega \text{ corresponds to } \frac{C_p^2}{2p+1}.$$

This substitution suffices to generalize (30), (31), and the result is in harmony with that formerly given.

The expression for the capacity (30) may be tested on the case of the planetary ellipsoid of revolution for which the solution is known [*]. Here $C_2 = \frac{1}{3}e^2$, e being the eccentricity. It must be remembered that a in (30) is not the semi-axis major, but the spherical radius of equal volume. In terms of the semi-axis major (α), the accurate value of the capacity is $\alpha e/\sin^{-1} e$.

We may now proceed to include the terms of the next order in C. The extension of (25) is

$$u_0^n H_n/H_0 = -C_n + \frac{1}{2}(2n+1) \int_{-1}^{+1} d\mu \, P_n \{C_1 P_1 + \ldots + C_p P_p\}$$
$$\{2C_1 P_1 + \ldots + (q+1) C_q P_q\}, \quad (33)$$

where in the small term the approximate value of H_n from (25) has been substituted. We set

$$\int_{-1}^{+1} d\mu \, P_n \{C_1 P_1 + \ldots + C_p P_p\}$$
$$\{2C_1 P_1 + \ldots + (q+1) C_q P_q\} = J_n, \quad (34)$$

where J_n is of order C^2 and depends upon definite integrals of the form

$$\int_{-1}^{+1} P_n P_p P_q \, d\mu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

n, p, q being positive integers.

In like manner the extension of (26) is

$$\phi_1/Qu_0 = 1 - \frac{2}{3}C_1^2 - \frac{3}{5}C_2^2 - \ldots - \frac{p+1}{2p+1} C_p^2$$
$$+ \frac{1}{2}\{2C_1 J_1 + 3C_2 J_2 + 4C_3 J_3 + \ldots\}$$
$$- \frac{1}{2} \int_{-1}^{+1} d\mu (C_1 P_1 + C_2 P_2 + \ldots)^2 \{C_1 P_1 + 3C_2 P_2 + \ldots$$
$$+ \frac{1}{2}p(p+1) C_p P_p\}. \quad . \quad . \quad . \quad (36)$$

Here, again, the definite integrals required are of the form (35).

* Maxwell's 'Electricity,' § 152.

These definite integrals have been evaluated by Ferrers [*] and Adams [†]. In Adams' notation $n+p+q=2s$, and

$$(35) = \frac{2}{2s+1} \frac{A(s-n) \cdot A(s-p) \cdot A(s-q)}{A(s)}, \quad . \quad . \quad (37)$$

where

$$A_n = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{1 \cdot 2 \cdot 3 \ldots n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

In order that the integral may be finite, no one of the quantities n, p, q must be greater than the sum of the other two, and $n+p+q$ must be an even integer. The condition in order that the integral may be finite is less severe than we found before in the two dimensional problem, and this, in general, entails a greater complication.

But the case of a single term in δu, say $C_p P_p(\mu)$, remains simple. In (36) J_n occurs only when multiplied by C_n, so that only J_p appears, and

$$J_p = (p+1) C_p^2 \int P_p^3 d\mu. \quad . \quad . \quad . \quad . \quad (39)$$

Thus (36) becomes

$$\phi_1/Qu_0 = 1 - \frac{p+1}{2p+1} C_p^2 + \frac{(p+1)(p+2)}{4} C_p^3 \int_{-1}^{+1} P_p^3 d\mu. \quad . \quad . \quad (40)$$

When p is odd, the integral vanishes, and we fall back upon the former result ; when p is even, by (37), (38),

$$\int_{-1}^{+1} P_p^3 d\mu = \frac{2}{3p+1} \frac{\{A(\tfrac{1}{2}p)\}^3}{A(\tfrac{3}{2}p)}. \quad . \quad . \quad (41)$$

For example, if $p=2$,

$$\int_{-1}^{+1} P_2^3 d\mu = \frac{4}{35},$$

and

$$\phi_1/Qu_0 = 1 - \tfrac{3}{5}C_2^2 + \frac{12}{35} C_2^3. \quad . \quad . \quad (42)$$

Again, if two terms with coefficients C_p, C_q occur in δu, we have to deal only with J_p, J_q. The integrals to be evaluated are limited to

$$\int P_p^3 d\mu, \quad \int P_p^2 P_q d\mu, \quad \int P_p P_q^2 d\mu, \quad \int P_q^3 d\mu.$$

If p be odd, the first and third of these vanish, and if q

* ' Spherical Harmonics,' London, 1877, p. 156.
† Proc. Roy. Soc. vol. xxvii. p. 63 (1878).

be odd the second and fourth.   If p and q are both odd, the terms of the third order in C disappear altogether.

As appears at once from (34), (36), the last statement may be generalized.   However numerous the components may be, if only odd suffixes occur, the terms of the third order disappear and (36) reduces to (26).

January 20, 1916.

XXVII. *Free Electrons in Gases.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the May number of the 'American Journal of Science' I published a brief account of the results of certain experiments dealing with the motion of ions and electrons through dry air : it was shown that the electrons remained free during their motion through the gas and that their relative number increased with diminution of pressure, the electrons coming into evidence in my experiments at about 8 cm. pressure.   These results were found to contain the explanation of the apparently anomalous increase of the mobility of the gas ion at reduced pressures ; when the ions were considered apart from electrons, the mobility remained normal throughout.

The existence of free electrons in gases at relatively high pressures had previously been demonstrated by Franck for argon, helium, and nitrogen at atmospheric pressure; it was found by him that when these gases were carefully freed from impurities (especially oxygen) the negative carriers were practically all electrons ; the slightest trace of oxygen, however, was sufficient to convert the carriers into ions. This ability to contain electrons in the free state was regarded as being a peculiarity exhibited by the inert gases ; the demonstration of their existence in air, which was indeed so *à priori* improbable on account of the presence of the electro-negative constituent oxygen, rendered it at once evident that Franck's result was a particular case of a more general principle, and that the free electrons along with ions would be found for all the ordinary gases, the inert gases being conspicuous by reason of their reluctance to form negative ions.

Immediately after the preliminary publication I resumed the experimental work ; this was completed last July, but,

owing mainly to the time involved in travelling, considerable delay has arisen in publishing the new results. I think it therefore advisable to make this brief communication, dwelling especially on certain features of the subject which it appears to me should be given prominence if satisfactory progress is to be made.

The free electrons were investigated for the gases carbon monoxide, carbon dioxide, and hydrogen ; for the two latter gases the electrons were considerably more numerous than in air at the corresponding pressure, a fact which was consistent with the result that the abnormal increase in the ionic mobility set in for these gases at higher pressures than for air. In hydrogen, the electrons appeared in considerable numbers at atmospheric pressure. A number of vapours were tried, but for the most part they showed no evidence of free electrons ; however, in these cases there was always a pressure of several mm., and it is quite possible that lower pressures would bring them into evidence. An interesting and remarkable exception is the vapour of petroleum ether (a mixture of pentane and hexane); for this vapour, whose molecules contain only atoms of carbon and hydrogen, the negative carriers appeared to consist entirely of electrons, the negative ions being absent : the vapour was, however, particularly sensitive to impurities, and, after standing for a few hours in a closed metallic vessel, would no longer contain any considerable number of free electrons.

I desire here to make some remarks with regard to the effect of impurities on the relative number of free electrons and negative ions in a gas : this is a point on which there exists considerable misapprehension. Franck found that the free electrons in the inert gases were especially sensitive to oxygen as an impurity. In the October number of the Philosophical Magazine Mr. Haines has stated the existence of free electrons in nitrogen and hydrogen at atmospheric pressure, and has mentioned oxygen as one of the impurities which if present in small amount would rob the former gas of its free electrons. Mr. Haines does not enter into detail with regard to the impurities in hydrogen, but I have myself found that a small quantity of oxygen in hydrogen at atmospheric pressure would deprive this gas of its electrons. It has probably appeared to many to be extremely strange that a trace of oxygen could have this effect and yet that free electrons should exist in air at several cm. pressure. As a matter of fact, the difficulty is more apparent than real. Although the results to which reference has just been made are perfectly correct, still, when the subject is viewed more

generally, the electrons are not sensitive to oxygen as an impurity. To consider only the case of hydrogen, as I did not experiment with the inert gases : I found that as the pressure was reduced the sensitivity to oxygen was markedly decreased; *e. g.*, to take actual figures, although a small amount of air (less than 1 mm. pressure) would rob hydrogen at 1 atmosphere of its free electrons, the electrons existed in considerable numbers in a mixture of hydrogen at $82\frac{1}{2}$ mm. and air at $2\frac{1}{2}$ mm. At still lower pressures it was found possible to increase the number of electrons by adding small amounts of air ; this arose from the extra number of electrons supplied by the air more than compensating for the diminution in the number supplied by the hydrogen.

For the explanation of these results, and indeed of many diverse results that have arisen during the course of the experiments, I have been constantly guided by the following idea, which has proved of the greatest assistance even should it subsequently be found not to correspond with reality: viz., that an electron cannot effect a permanent union with an uncharged molecule to form a negative ion unless the relative velocity at collision exceed a critical value characteristic of the molecule concerned ; in other words, there is a definite potential of ion formation just as there is a definite ionization potential, the former of course being smaller than the latter, probably of the order of one half.

To revert to the case of hydrogen with oxygen as the impurity. If an electron be expelled from a hydrogen molecule, we can imagine a sphere A drawn round the parent molecule of such a radius that the electron will be effective in forming a negative ion for any collision with a hydrogen molecule within this sphere ; also a sphere B of larger radius corresponding to the formation of a negative oxygen ion. Now in pure hydrogen the free electrons that are observed are those which pass the boundary of the sphere A ; if a trace of oxygen be present, an electron may form a negative oxygen ion in the region between A and B. In hydrogen the electrons must have at collision a fairly high degree of elasticity, so that we may regard the velocity of the electron between A and B as being approximately a function of its distance from the parent molecule. Now the chance of meeting an oxygen molecule between A and B is much greater if the hydrogen be at a high than at a low pressure, because in the former case the time taken for the electron to cross the region is considerably greater owing to the larger number of collisions. The sensitivity of the

electronic effect to traces of oxygen increases, therefore, over a wide range with the pressure of the hydrogen.

An interesting question arises as to whether in the case of certain vapours the electron has sufficient energy at ordinary temperatures to form with a molecule a negative ion : in such cases permanently free electrons would not be possible except with field strengths high enough to effect ionization by collision. I was not able to make a systematic study of vapours at low pressures to ascertain whether free electrons did really exist, but an examination of the decay of the free electrons in petroleum ether vapour as ageing occurred, indicated the appearance in the vapour of another constituent capable of absorbing electrons at ordinary temperatures. This arose probably from the walls of the containing vessel, although the possibility of a formation of aggregates by the vapour molecules themselves has to be considered. In any event these "electron sinks" undoubtedly exist, and should be carefully distinguished as regards their effect upon electrons from impurities such as oxygen.

The study of the free electrons in various gases is one of great importance and should repay careful investigation. They are really observable in practice, especially if a high-frequency commutator be employed ; elaborate precautions are not necessary if it be merely required to bring the electrons into evidence—*e. g.*, in my preliminary experiments I was able to observe the electrons in considerable numbers at atmospheric pressure, in hydrogen which was prepared from commercial acid and zinc in a Kipp's generator and dried in the usual way before passing into the apparatus.

What is urgently needed is a determination of the proportion of ions and electrons in a pure gas at a specified pressure ; to say that the electrons occur in air at 8 cm. or in hydrogen at 1 atmosphere provides little information, because the sensitivity of the measuring apparatus is involved. A case of particular interest would be to ascertain whether any negative ions are present in pure inert gases, as a small proportion of ions might not unreasonably be expected.

I hope within a few months to be able to publish the full account of my work.

Yours very truly,

E. M. Wellisch.

The University,
　Sydney,
　　December 22nd, 1915.

XXVIII. *On Two-Dimensional Fields of Flow, with Logarithmic Singularities and Free Boundaries.* By J. G. LEATHEM, *M.A., D.Sc.**

1. *INTRODUCTION.*—In a recently published paper †
the writer has defined conformal curve-factors,
discussed some of their properties, and employed them in
the solution of problems of two-dimensional liquid flow. In
all the configurations there discussed the fixed boundary has
been an open polygon, rectilineal or partly curvilinear,
whose continuity is not broken at any point, and the field
has been free from singularities. It is now proposed to
show how the same calculus may be applied to regions
whose fixed boundary is broken and to fields which contain
logarithmic singularities, as, for example, to cases of liquid
flow between two boundary stream-lines and cases of flow
due to sources or vortices.

Methods of solving problems of this kind, with a special
view to the determination of the forms of free stream-lines,
have been given by Mr. J. W. Michell ‡, Prof. A. E. H.
Love §, and Prof. B. Hopkinson ∥, who all deal with cases in
which the fixed parts of the boundary are rectilineal polygons.
It will be shown that the method of curve-factors deals with
such problems in a different and more concise manner, and
is further applicable to some cases in which part of the fixed
boundary is curvilinear. The analysis is, of course, capable
of interpretation in terms of fields of electric flow or force,
and it is believed that the method of curve-factors may be
regarded as a comprehensive mode of approaching all those
classes of physical problems which can be formulated in
terms of conformal transformation.

2. *Double transformation.*—The general problem is that of
determining a relation between two fundamental complex
variables, namely, $z \equiv x + iy$ the variable of the geometrical
configuration, and $w \equiv \phi + i\psi$ the variable specifying the
field of flow or force (the velocity being the vectorial rate of
decrease of ϕ). When the field is free from singularities

* Communicated by the Author.

† "Applications of Conformal Transformation to Problems in Hydro-
dynamics," R. S. Phil. Trans., sec. A, vol. ccxv. (1915).

‡ "The Theory of Free Stream-Lines," R. S. Phil. Trans., sec. A,
vol. clxxxi. (1890).

§ "The Theory of Discontinuous Fluid Motions," Proc. Camb. Phil.
Soc. vol. vii. (1891).

∥ "Discontinuous Fluid Motions involving Sources and Vortices,"
Proc. Lond. Math. Soc. vol. xxix. (1898).

what is wanted is a conformal representation of the relevant region in the z plane on the half-plane of w for which ψ is positive; but when there are singularities the (z, w) relation is not conformal, and an intermediate variable $\zeta \equiv \xi + i\eta$ is introduced, and relations are established between z and ζ, and between w and ζ. The (z, ζ) relation is a conformal representation of the relevant region in the z plane upon that half-plane of ζ for which η is positive, and is generally a differential relation formulated in terms of Schwarzian factors and curve-factors by the methods, and subject to the limitations, explained in the previous paper. The (w, ζ) relation is an explicit formula for w in terms of ζ, constructed by taking account of the specified singularities, with such images as are required to make $\psi = 0$ when $\eta = 0$. The difficulty of integration, inevitable in problems of this kind, arises only in connexion with the (z, ζ) relation.

3. *The geometrical relation.*—In constructing the (z, ζ) relation it is to be noted that a gap in the boundary at infinity, corresponding to the parallelism or divergence of two parts of the boundary, is to be regarded as a corner and dealt with by means of a suitable Schwarzian factor. Curves in the fixed part of the boundary are represented by curve-factors selected from known types of suitable angular range, and these curve-factors (unfortunately not usually the curves themselves) are among the data of the problem. Curves which are free stream-lines are represented by curve-factors which are among the quæsita of the problem.

4. *The field relation.*—In constructing the (w, ζ) relation a distinction must be drawn between singularities in the boundary and singularities at other points of the field. The only singularities contemplated are logarithmic, namely, in cases of liquid flow, sources and vortices, doublets being got by differentiation if desired. A source in the boundary at the point $\zeta = c$, whose rate of output into the field is m, is represented in w by a term $-(m/\pi) \log (\zeta - c)$. A vortex in the boundary is inadmissible since it involves an infinity of ψ.

If the point $\zeta = c$ corresponds to a point at infinity in the z plane, the singularity represented by the above term is a source at infinity, that is an influx of liquid at the rate m through an infinitely distant gap in the boundary.

A source whose rate of output is m, situated in the field at a point $\zeta = \alpha + i\beta$, must be counterbalanced by an image source at the point $\zeta = \alpha - i\beta$. Hence it is represented in w by a term
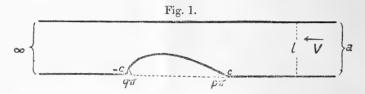
$$-(m/2\pi) \log \{(\zeta - \alpha - i\beta)(\zeta - \alpha + i\beta)\}. \quad . \quad . \quad (1)$$

Similarly a vortex at the point $\zeta = \gamma + i\delta$, round which the circulation is μ, is represented in w by a term

$$(i\mu/2\pi) \log \{(\zeta - \gamma - i\delta)/(\zeta - \gamma + i\delta)\}. \quad . \quad . \quad (2)$$

5. *Motion of a ship in a canal.*—As a first example one may consider the case of a doubly pointed ship moving along the central line of a uniform straight canal. On superposition of a motion equal and opposite to that of the ship, the ship becomes part of the fixed boundary. Only half the configuration need be studied, and the z diagram is as shown in fig. 1, wherein the values assigned to ζ at the important

Fig. 1.

points are indicated. The angles at bow and stern are taken to be $2p\pi$ and $2q\pi$.

The velocity at infinite distance being V, there is a source of output lV at $\zeta = a$, and an equal sink at $\zeta = \infty$. The geometrical and field relations are

$$dz = \frac{-\mathrm{E}\mathscr{C}(\zeta)d\zeta}{(\zeta + c)^q(\zeta - c)^p(\zeta - a)}, \quad w = -\frac{l\mathrm{V}}{\pi} \log (\zeta - a), \quad . \quad . \quad (3)$$

where E is a positive constant and $\mathscr{C}$ is a curve-factor in ζ, having linear range from $-c$ to c, and angular range $(p + q)\pi$. The curve-factor $\mathscr{C}$ may be any one of several known types, and the shape of the ship depends on the form of $\mathscr{C}$ and the values of all parameters in the geometrical relation.

One condition which the parameters must satisfy corresponds to the geometrical relation giving the proper breadth to the canal at $\zeta = a$ and $\zeta = \infty$. The abrupt changes in the value of y indicated by this relation lead to

$$\frac{\pi \mathrm{E}\mathscr{C}(a)}{(a + c)^q(a - c)^p} = l = \pi \mathrm{E} \lim_{\zeta \to \infty} \left\{ \frac{\mathscr{C}(\zeta)}{(\zeta + c)^q(\zeta - c)^p} \right\} \quad . \quad (4)$$

Thus, for example, if the selected curve-factor be

$$\mathscr{C} = \mathscr{C}_9^{p+q} = \{\lambda(\zeta - k) + (\zeta - c)^a(\zeta + c)^{1-a}\}^{p+q} \quad . \quad . \quad (5)$$

it is necessary that

$$\{\lambda(a - k) + (a - c)^a(a + c)^{1-a}\}^{p+q}(a + c)^{-q}(a - c)^{-p} = (\lambda + 1)^{p+q}.$$

6. *Effective inertia of a ship in a canal.*—A compact formula for the longitudinal inertia-coefficient of the ship (assumed to have the same mass as the liquid which it displaces) can be deduced. If X is the impulse required to set up a motion of the ship with velocity V in still water of density ρ, it can be shown that

$$\rho^{-1}X = \Sigma \pm \int_{-l}^{l} (\phi - x \partial\phi/\partial x) dy, \quad . \quad . \quad . \quad (6)$$

the summation referring to two straight lines of integration across the canal, one (with sign $+$) ahead of the ship, the other (with sign $-$) astern.

To right and to left w can be expanded in the forms

$$Vz + c_0 + \Sigma c_n \exp(-n\pi z l^{-1}), \quad Vz + c_0' + \Sigma c_n' \exp(n\pi z l^{-1}), \quad (7)$$

where the n's are integers. Only the terms c_0 and c_0' contribute to the limit of the right-hand side of (6) when the transverse lines tend to infinite remoteness. Hence

$$\rho^{-1}X = 2l(c_0 - c_0') = -2l \int_{\zeta=a}^{\zeta=\infty} (dw - V dz), \quad . \quad . \quad (8)$$

wherein the subject of integration is supposed to be expressed in terms of ζ by means of formulæ (3).

7. *Electrical flow in a flat conducting strip pierced by a symmetrical hole.*—The analysis of the previous article may be interpreted in terms of two-dimensional electric flow, ϕ being taken to be the product of the electric potential and the constant specific conductivity, and the " ship " being represented by a hole cut in the strip.

In this state of flow let dz_1 be the element of geometrical displacement corresponding to $d\phi$ when $\psi = 0$; and let dz_2 be the corresponding element in what would be the flow if there were no hole in the strip, in which case dw would equal $V dz$. Then

$$\int_a^\infty \left\{ \frac{l\pi^{-1}}{\zeta-a} - \frac{E\mathscr{E}(\zeta)}{(\zeta+c)^q(\zeta-c)^p(\zeta-a)} \right\} d\zeta = \int_{\zeta=\infty}^{\zeta=a} (dz_2 - dz_1), \quad (9)$$

and the latter integral represents the limit of the difference between the lengths of the strip, with and without the hole, which correspond to the same difference of potential. In fact it represents the increase of the ohmic resistance of the strip, due to the presence of the hole, in terms of the resistance per unit length.

Any distribution of electrodes, symmetrical about the central line of the strip, can be dealt with by introducing into w terms of the type of formula (1).

8. *Liquid flow with free stream-lines, with or without sources and vortices.*—When the fixed part of the boundary is a rectilineal open polygon the (z, ζ) relation is

$$dz = \mathscr{E}(\zeta)\mathrm{F}(\zeta)d\zeta,$$

where $\mathrm{F}(\zeta)$ is a product of Schwarzian factors determined in the usual manner, and $\mathscr{E}(\zeta)$ is an as yet unknown curve-factor representing the free boundary. The problem is reduced to quadrature when the form of $\mathscr{E}$ has been ascertained, and it will now be shown how $\mathscr{E}$ is determined from the condition that $|\,dz/dw\,|$ is constant in the free boundary. The field relation is of the type

$$w = \mathrm{A}\zeta - \Sigma\frac{m}{2\pi}\log\{(\zeta-\alpha)^2 + \beta^2\} + \Sigma\frac{i\mu}{2\pi}\log\left\{\frac{\zeta-\gamma-i\delta}{\zeta-\gamma+i\delta}\right\}, \quad (10)$$

so that $dw/d\zeta$ is an algebraic fraction in ζ of known form ; and $dz/dw = \mathscr{E}\mathrm{F}d\zeta/dw$. The modulus of this can be made constant in the linear range of $\mathscr{E}$ by building up $\mathscr{E}$ by factors, each factor being itself a curve-factor of such a character that, when it is associated with a particular factor in numerator or denominator of $\mathrm{F}d\zeta/dw$, the combination has (for values of ζ corresponding to the free boundary) a modulus independent of ζ. Every factor of $\mathrm{F}d\zeta/dw$ being dealt with in this way, the complete product of the curve-factors is $\mathscr{E}$.

If the algebraic sum of the outputs of the given sources, including a possible source at infinity of output $\pi\mathrm{A}$, is not zero, the free stream-line will extend to infinity. In this case the linear range may be taken from $\zeta = -\infty$ to $\zeta = 0$, and the synthesis of $\mathscr{E}$ is as follows :—(i.) A factor $(\zeta-a)^n$, where a is real and positive, occurring in $\mathrm{F}d\zeta/dw$, is to be associated with $\mathscr{E}_{13}^{-2n}$, where $\mathscr{E}_{13} \equiv a^{1/2} + \zeta^{1/2}$, which is known to be a curve-factor of the assigned linear range with modulus $(a-\zeta)^{1/2}$ in that range. (ii.) A product of conjugate complex factors $\{(\zeta-\alpha)^2 + \beta^2\}$ may occur in the denominator of $d\zeta/dw$, and will certainly occur in the numerator if there are sources or vortices clear of the boundary. Now

$$\mathscr{E}_{51} \equiv \zeta + (\alpha^2 + \beta^2)^{1/2} + \{2(\alpha^2 + \beta^2)^{1/2} + 2\alpha\}^{1/2}\zeta^{1/2} \quad (11)$$

is a curve-factor having the assigned linear range, with modulus $\{(\zeta-\alpha)^2 + \beta^2\}^{1/2}$ in that range. Hence

$$\mathscr{E}_{51}^{-2}\{(\zeta-\alpha)^2 + \beta^2\}$$

has constant modulus. (iii.) There may occur in the denominator of $d\zeta/dw$ a factor $\zeta+b$, where b is positive. This vanishes at a point in the linear range, and it is impossible for a proper curve-factor to have a modulus which vanishes in its linear range. Hence the only way of maintaining constancy of modulus of dz/dw, so far as this element is concerned, is to introduce into $\mathscr{E}$ a similar factor $\zeta+b$. This is a corner-factor, and introduces a corner of internal angle 2π into the free stream-line; in fact it represents a cusp in the free boundary, pointing inwards to the field. If b were zero one branch of the cusp would belong to the fixed boundary.

Thus $\mathscr{E}$ is completely determined as a product of powers of terms of the type of $\mathscr{E}_{13}$, $\mathscr{E}_{51}$, and $(\zeta+b)$.

If the free boundary does not extend to infinity the linear range of $\mathscr{E}$ must be finite, and may be taken from $\zeta=-c$ to $\zeta=c$; and the synthesis of $\mathscr{E}$ is as follows :—(i.) If a factor $(\zeta-a)^n$, where $a^2>c^2$, occurs in $\mathrm{F}d\zeta/dw$, put $a=c\cosh\gamma$, and note that

$$\mathscr{E}_6 \equiv \zeta-ce^{-\gamma}+(\zeta^2-c^2)^{1/2} \quad . \quad . \quad . \quad . \quad (12)$$

is a curve-factor whose modulus in its own range is

$$\{2ce^{-\gamma}(c\cosh\gamma-\zeta)\}^{1/2}.$$

Thus $\mathscr{E}_6^{-2n}(\zeta-a)^n$ has constant modulus, and $\mathscr{E}_6^{-2n}$ is the proper factor to be introduced into $\mathscr{E}$. A particular case of $\mathscr{E}_6$ is $\mathscr{E}_1 \equiv \zeta+(\zeta^2-c^2)^{1/2}$, whose modulus in its own linear range is constant. The apparent possibility of introducing into $\mathscr{E}$ any arbitrary power of $\mathscr{E}_1$ might seem to indicate indeterminateness of $\mathscr{E}$, but the power of $\mathscr{E}_1$ is not arbitrary, being determined by consideration of the angular range of the (z, ζ) transformation. (ii.) A pair of conjugate complex factors $\{(\zeta-\alpha)^2+\beta^2\}$ occurring in $d\zeta/dw$ is counterbalanced by introducing into $\mathscr{E}$ a suitable power of a factor of the type

$$\mathscr{E}_7 \equiv (\zeta-k)\cosh\gamma+(\zeta^2-c^2)^{1/2}\sinh\gamma \quad . \quad . \quad (13)$$

The parameters are determined by the relations

$$\cosh\gamma=\big[\{(\alpha+c)^2+\beta^2\}^{1/2}+\{(a-c)^2+\beta^2\}^{1/2}\big]/2c, \quad k=\alpha/\cosh^2\gamma,$$

and the modulus of $\mathscr{E}_7$ in its own linear range is

$$\{(\zeta-\alpha)^2+\beta^2\}^{1/2}.$$

(iii.) If the denominator of $d\zeta/dw$ contains a factor $\zeta-b$, where $c^2>b^2$, the same factor (a corner factor) must be introduced into $\mathscr{E}$. This indicates an inward-pointing cusp in the free boundary.

The angular range which the (z, ζ) transformation must have is known from inspection of the fixed boundary; it is generally $-\pi$. As the angular range is π times the order at infinity of $dz/d\zeta$, there can be no uncertainty about the power of $\mathscr{E}_1$ which must be introduced into $\mathscr{E}$ in order to give the desired angular range. Thus the synthesis of $\mathscr{E}$ in terms of $\mathscr{E}_6$, $\mathscr{E}_1$, $\mathscr{E}_7$, and corner factors, is determined.

When there is flow to infinity between two free stream-lines which tend to parallelism, one factor is employed to represent the double curve. The linear range is taken from $\zeta = c$ through $\zeta = +\infty$ and $\zeta = -\infty$ to $\zeta = -c$. Two forms of curve-factor, namely,

$$\mathscr{E}_{52} \equiv (\zeta + k) \sinh\gamma - i(\zeta^2 - c^2)^{1/2}, \quad \mathscr{E}_{53} \equiv (k - \zeta) \sinh\gamma - i(\zeta^2 - c^2)^{1/2}, \quad (14)$$

where $k > c$, can be adapted to counterbalance the variability of modulus of real or pairs of imaginary factors in $Fd\zeta/dw$; it is unnecessary to go into details of the algebra.

As an example consider the case in which the fixed boundary consists of a semi-infinite and a finite straight line meeting at right angles, and the motion is due to a single source. The transformations are

$$dz = \frac{-\mathrm{E}\mathscr{E}d\zeta}{(\zeta - c)^{1/2}}, \quad w = -\frac{m}{2\pi} \log\{(\zeta - \alpha)^2 + \beta^2\}, \quad . \quad (15)$$
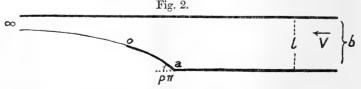
whence

$$dw/d\zeta = -(m/2\pi)(\zeta - \alpha)\{(\zeta - \alpha)^2 + \beta^2\}^{-1}.$$

The rules of synthesis indicate that

$$\mathscr{E} = (c^{1/2} + \zeta^{1/2})(\alpha^{1/2} + \zeta^{1/2})^2 \mathscr{E}_{51}^{-2} \text{ or } (c^{1/2} + \zeta^{1/2})(\zeta - \alpha)\mathscr{E}_{51}^{-2}, \quad (16)$$

according as α is positive or negative.

9. *Free stream-line problems in which part of the fixed boundary is curved.*—The possibility of specifying solvable problems of this type may be illustrated by the case of flow through a semi-infinite straight pipe with a symmetrical curved nozzle. Fig. 2 shows half the configuration (which

Fig. 2.

is all that need be considered), and the values assigned to ζ at the various points. The transformations are of the form

$$dz = \frac{-\mathrm{E}\mathscr{E}d\zeta}{(\zeta - a)^p(\zeta - b)}, \quad w = -\frac{l\mathrm{V}}{2\pi} \log(\zeta - b), \quad . \quad (17)$$

so that $dz/dw \propto \mathscr{E}(\zeta-a)^{-p}$. It is required of $\mathscr{E}$ that it be a curve-factor having linear range from $\zeta = -\infty$ to $\zeta = a$, angular range $p\pi$, and such that $| \mathscr{E}(\zeta-a)^{-p} |$ is constant for negative values of ζ.

Forms of $\mathscr{E}$ known to satisfy these conditions are

$$(\zeta^{1/2}+a^{1/2})^{2p}\mathscr{E}_{31}^{\lambda} \quad \text{and} \quad \mathscr{E}_{34}^{2p}, \text{ where}$$

$$\mathscr{E}_{31} \equiv \{(\zeta^{1/2}+a^{1/2})/(\zeta^{1/2}-a^{1/2})\}^{\sqrt{a}}\{(\zeta-a)/\zeta\}^{\sqrt{\zeta}}, \quad . \quad . \quad (18)$$

$$\mathscr{E}_{34} \equiv (\zeta^{1/2}+a^{1/2})^{(\zeta+a)/2a}(\zeta-a)^{(\zeta-a)/4a}\exp(-\tfrac{1}{2}\zeta^{1/2}a^{-1/2}). \quad (19)$$

Other forms of curve-factor which can be used in this way may be got by assigning convenient forms to f in the formula

$$\mathscr{E}_{30} = \operatorname{Exp} \pi^{-1}\int_0^a f'(\theta) \log \{(\zeta^{1/2}+\theta^{1/2})/(\zeta^{1/2}-\theta^{1/2})\}d\theta, \quad . \quad (20)$$

or by using another formula given in article 40 of the previous paper on the subject. In each case the form of the nozzle depends upon the selected form of $\mathscr{E}$. The difficulty of integrating the (z, ζ) relation may be formidable.

XXIX. *The Determination of the Work Function when an Electron escapes from the Surface of a Hot Body. By* HORACE H. LESTER [*].

THE equation for the thermionic emission from a hot metal in a vacuum has been deduced by Richardson [†] and others from theoretical considerations involving the assumption that the potential energies of an electron inside and outside of the surface are different, so that an escaping electron must do work against an equivalent adverse potential difference. This difference in potential is represented in equivalent volts by the symbol ϕ. The work done by an escaping electron is represented in the well-known Richardson equation

$$i = a\theta^{\frac{1}{2}}e^{-\frac{b}{\theta}}$$

by the constant b.

In order to justify completely the assumption involved in b, such a work function should be found to exist, and its magnitude should be identical with that of b.

In 1903 Richardson [‡] showed that the escape of electrons

should involve a loss of thermal energy, due to the fact that energy is rendered latent by the potential difference at the surface, and that this loss ought to increase rapidly with the temperature. Wehnelt and Jentzsch[*] announced the discovery of such a cooling effect, and attempted its measurement. However, they seem to have neglected to compensate for the disturbing action of the thermionic current in their bridge system, so that the effect they measured was considerably obscured by the thermionic current disturbances. Cooke and Richardson[†] found such an effect in 1913. They described a method of measurement, and published values on the cooling effect, for osmium and tungsten. Before this, however, viz. in 1910, the same experimenters had announced the discovery of a converse heating effect[‡] and had published values for a series of metals. The value of ϕ was calculated from both the heating and the cooling effects, and was found to be of the expected order of magnitude.

The present paper contains a discussion of their work on the heating effect, and presents an extension of their measurements of the cooling effect. Some related features are discussed. The paper is divided as follows :—

I. Experiments of Richardson and Cooke.

II. Measurement of the cooling effect for carbon, molybdenum, tantalum, and tungsten.

III. Related features :
    1. Identification of b with ϕ.
    2. Relation of ϕ to contact potentials.
    3. Effect of gases on ϕ.
    4. Nature of surface films.
    5. A new method for determining the temperatures of hot filaments.

I. Experiments of Richardson and Cooke.

These experiments carried out in this laboratory showed the existence of the heating effect. It is not claimed for them that they show more than the order of magnitude. In fact, Richardson was inclined to the view that, owing to the way in which the contact potential entered, the effect found rather measured the cooling effect at the surface of the hot

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[*] *Ann. der Physik,* (3) vol. xxviii. p. 537 (1909).
[†] Phil. Mag. April and Sept. 1913.
[‡] Phil. Mag. July 1910 and April 1911.

electrode than the heating effect at the surface of the cold one *.

The rate of production of heat by a current i flowing across the boundary of the cold electrode is given as

$$i\left(\phi + \mathrm{V} + \frac{\alpha}{e}(\theta_1 - \theta_0)\right),$$

where ϕ represents the equivalent potential at the surface,
V the potential between the electrodes,
α twice the gas constant calculated for a single molecule,
e the charge on an electron,
θ_1 and θ_0 the absolute temperatures of the hot and cold electrodes respectively.

i is the saturation current and is independent of V. The θ's are constant; hence the expression inside the parentheses is a linear function of V. The heating effect was measured by comparing the change in resistance produced by the influx of electrons with that produced by a known increment of current through the metal of the electrode. The effects thus found for a series of voltages were plotted against V, and the intercept of the straight line thus found with the heating-effect axis gave the value per unit current of

$$\phi + \frac{\alpha}{e}(\theta_1 - \theta_0) = \mathrm{H} ;$$

from which

$$\phi = \mathrm{H} - \frac{\alpha}{e}(\theta_1 - \theta_0).$$

The materials under investigation were mounted in thin strips forming a grid between two osmium filaments which served as the hot cathode. The electrodes were mounted in a brass vessel that was made airtight by means of waxed joints. It was impossible to observe in such an arrangemnt the precautions that Langmuir has since shown to be necessary to insure consistent behaviour of thermionic phenomena.

Their results showed that small changes in the gas-pressure did not affect the value of ϕ. Evidence was found to support a theory put forth by Richardson that the heating effect is a function of the cooling effect through the relationship

$$\mathrm{W}_1 = \mathrm{W}_2 + e\mathrm{V}_c,$$

or in terms of ϕ,

$$\phi_1 = \phi_2 + \mathrm{V}_c,$$

where V_c represents the contact potential between the hot

* O. W. Richardson, "Rapports du Congrès Int. de Radiologie," Brussels, 1910.

and cold electrodes, ϕ_1 the cooling effect at the hot, and ϕ_2 the heating effect at the cold electrode.

Langmuir has shown that the big effects due to the presence of residual gases disappear only with the last traces of the gases * ; hence, in view of the lack of ideal conditions, it is not surprising that Richardson and Cooke did not find that changes in gas-pressure affect the heating effect.

The dependence of the heating effect of the anode upon the cooling effect of the cathode was shown by some peculiar results obtained in experiments with osmium as the source of the thermions and iron as the receiving surface. It was found that the osmium developed two ranges of thermionic emission; *i. e.*, for a given temperature two values of the saturation current were possible. Apparently two values of ϕ were involved. The larger saturation current gave larger values of the heating effect, and the lower saturation current gave lower values of the heating effect.

The theory of the dependence of the heating upon the cooling effect regards the work done when an electron is taken completely around the circuit. If W_1 and W_2 represent the work-functions at the surfaces of the hot and cold electrodes respectively, and if V_c is the contact-potential between the two metals, then this work may be expressed as

$$W_1 - eV_c - W_2 + \psi = 0,$$

where ψ includes work done against external resistance, gas pressure, and Peltier potential. The terms in ψ are negligible in comparison with the first three; hence we have

$$W_1 = W_2 + eV_c. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

According to this relation, $(W_2 + eV_c)$ varies directly with W_1.

Now the thermionic currents at a given temperature vary inversely with b. Hence, since ϕ and b are supposed to be equivalent, it is evident that the observed change in the heating effect should have been inverse to the change in current; that is, $W_2 + eV_c$, the effect measured, should have been smaller for the larger current. This was contrary to their observation. It is possible that a contrary change in eV_c more than compensated for the change in W.

The same experimenters later measured the cooling effect

* Phys. Rev. Dec. 1913.

for osmium [*]. According to the theory given above, this should have been equal to the heating effects already measured. They found for the cooling effect at the osmium surface, 4·7 equivalent volts. The values in eq. volts for the series of metals whose heating effects were determined (omitting iron) were 7·26. 5·3, 7·1, 5·82, 5·6, 5·15, and 7·4, which gives a mean of 6·23. No one of the measurements gave a value as low as that obtained for the cooling effect of osmium, and the difference from the mean was 1·5 volts. It seems, therefore, that the experimental evidence does not verify the relation expressed in (1). Further reference to this discussion will be made when contact potentials are considered. It will be shown that the sign of V_c in equation (1) probably should be changed.

II. Measurements of ϕ from the Cooling Effect.

In 1913 Cooke and Richardson published experiments that showed conclusively the existence of the cooling effect, and described a method of measurement that is capable of giving quite accurate results. This method has been employed in the present investigation and will be described in some detail. Their rather lengthy mathematical deductions are omitted. For a complete discussion of the method the reader is referred to the original paper.

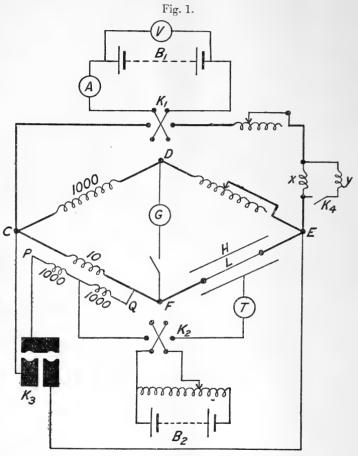The expression for the loss of thermal energy due to the escape of electrons is the same as that for the gain of thermal energy in the heating effect, viz.

$$i\left(\phi + \frac{\alpha}{e}(\theta_1 - \theta_0)\right).$$

The symbols have the same significance as before. The cooling effect, as in the former case, was measured by noting the change of resistance caused by the change in temperature (in the cathode in this case), and by comparing this change of resistance with that produced by a known change of electrical energy. The experimental arrangement is shown in fig. 1.

Battery B_1 supplied energy to a bridge network in one arm of which the filament was inserted. The other arms consisted of a 10-ohm Wolff standard, a 1000-ohm ratio-coil of a Leeds & Northrup bridge, and the variable resistance from the same bridge. The bridge current could be reversed by the commutator K_1, and could be increased by a very

[*] Phil. Mag. April 1913.

small fraction of itself by means of a 100-ohm shunt (y) around a 1-ohm cell (x) in series with the battery. These resistances were Wolff standards. The 1-ohm and the 10-ohm coils were maintained at constant temperature

Fig. 1.

by means of an oil-bath. A Weston ammeter (A), reading to 1500 milliamperes, served to measure the bridge current. It was compared with another ammeter for which the calibration was known. The battery potentials were read on a Weston voltmeter (V) reading to 75 volts. It was compared with a Weston standard voltmeter and found to agree. The standard was later calibrated by means of a Wolff potentiometer and a Weston normal cell.

The thermionic current was introduced into the bridge

system in either of two ways. In the first method it was introduced at the middle point of the arm CF by means of the high-resistance shunt PQ. In the second, the shunt was placed around the arm FE by means of the key K_3. With this arrangement the thermionic potentials were applied to the middle point of the filament L. The thermionic potentials were measured by means of the micro-ammeter, T. This instrument was a Paul testing set, giving 1 scale-division per 2 microamperes and reading up to 375×10^{-4} ampere by means of suitable shunts. It was calibrated by means of a Wolff potentiometer and a Wolff standard resistance. The thermionic potentials were supplied by a 120-volt storage battery, across which was shunted a 1500-ohm slide-wire resistance from which suitable potentials were tapped off. The potential used was ordinarily about 40 volts. The thermionic currents were started or stopped by reversing the commutator K_2. The galvanometer used was of the d'Arsonval type, with a resistance of 225 ohms, and gave a deflexion of 1 scale-division for a current of 9×10^{-9} ampere.

Method of Observation.

Observations were carried out as follows. The key K_3 was closed, so as to shunt the 10-ohm standard in the arm CF. With the thermionic current off, K_4 was opened and closed and the resulting galvanometer deflexions were recorded. Usually seven deflexions constituted a set. Then, with K_4 open and K_2 alternately reversed, the resulting deflexions due to turning the thermionic current on and off were recorded. From seven to fifteen deflexions were taken in this case, depending on the magnitudes of the deflexions and the steadiness of the galvanometer. The mean de-flexion was determined in most cases by the method described in Richardson and Cooke's first paper *. The ammeters A and T were read, the voltage of B_1 determined, and the resistance of L was read from the bridge system. K_1 was now reversed, and the whole system of measurements repeated. The two series of observations constituted one complete set for the "Standard Shunted" arrangement. An exactly similar complete set was taken with K_3 closed, so as to shunt the filament instead of the 10-ohm standard. This second set with the "Filament Shunted" arrangement gave the data for calculating an independent value of ϕ. The two methods gave consistent results.

* Phil. Mag. July 1910.

Theory of Measurements.

The methods consisted chiefly in comparing the loss of heat due to turning on the thermionic current with the gain in heat when a known increment of current was supplied to the filament. The comparison was effected by assuming that ∂H, the change in heat supplied to the filament, was in each case proportional to ∂R, the change in resistance of the filament. The increment of resistance due to an increase in the current was accomplished by shunting x with y. The final expression for the change in the supply of energy is given by the expression

$$\partial E = (1+q)^2 i_1^2 \left(2R . \frac{i_1 x^2}{x+y} . \frac{1}{v} + \partial R_e \right), \quad . \quad . \quad (2)$$

where

$$\partial R_e = 9 \times 10^{-9} . \frac{1+q}{i_1} \left(G + \overline{DE} \left(1 + q + \frac{G}{\overline{CD}} \right) \right) D_e, \quad . \quad . \quad (3)$$

where

∂E = increment of the rate of supply of energy;
q = fractional part of bridge-current through the high-resistance arms;
i_1 = current through the bridge;
R = resistance of the filament;
G = resistance of the galvanometer—225 ohms;
x = shunted portion of external resistance—1 ohm.
y = shunt about x—100 ohms;
∂R_e = change in resistance of the filament due to shunting x;
D_e = galvanometer deflexion due to shunting x;
$\overline{DE}$ and $\overline{CD}$ = resistances in the arms $\overline{DE}$ and $\overline{CD}$ respectively.

The change in the resistance due to starting the thermionic current is not so easily determined. The presence of the thermionic current in the bridge system disturbs the galvanometer balance, and there is a change in the resistance of the filament due to the Joule heating effect of the thermionic current. The first effect is minimized for the "standard shunted" method by introducing the thermionic current at the middle points of the two lower arms. With this arrangement the current should distribute itself symmetrically around the network and should not influence the galvanometer. For the "filament shunted" arrangement the current theoretically departs from and returns to the same point in the filament, and is not present as a disturbing factor in the bridge network. As a matter of fact, perfect compensation is not achieved in either case. In the first

case, the thermionic potentials are placed on one end of the filament. The superposition of the bridge current causes an unsymmetrical emission of electrons, so that the thermionic current is not quite symmetrically distributed about the bridge network. In the second case, the superposition of the bridge current causes a shift in the centre of emission from the centre of resistance to which point the current was returned, so that there is a resultant potential difference along the wire. These effects are supposed to reverse with the bridge current. With i first in one direction and then in the other, alternately, high and low values of ϕ may be obtained. The mean of these values is supposed to be the correct one.

In practice these two values are not worked out. The readings for the two values are grouped into a single equation, but the validity of the method depends upon the truth of the above assumption. Inasmuch as Cooke and Richardson did not test the above assumption experimentally, it was deemed advisable to perform such a test in this investigation. The two values of ϕ, found with i first in one direction and then in the other, differ by a considerable amount. If, however, an alternating current be used to heat the wire and a small superimposed direct current be used to operate the bridge, two values of ϕ should be found that differ by a much smaller amount. This experiment was performed, and the prediction was fulfilled. The two values found for the cooling effect were 4·742 and 4·797, the mean for the two being 4·766. Unfortunately, an accident prevented the securing of direct-current measurements on this particular filament. However, characteristic values from a similar filament by the direct-current method were 6·210 and 3·315, the mean being 4·763. The results of the experiment were regarded as satisfactory proof of the validity of the assumption that the mean of the high and the low values in the direct-current method really eliminated the uncompensated portion of the disturbance produced by the thermionic current in the bridge system.

The Joule heating effect of the thermionic current presents more difficulty. It cannot be eliminated and can be calculated only approximately. Cooke and Richardson performed this calculation and incorporated the correction term found in the general expression for the total diminution of energy due to the escape of electrons. They found for the total rate of loss the expression

$$\partial \dot{H} = T\left(\phi + \frac{\alpha}{e}(\theta_1 - \theta_0)\right) + Ri_1^2\left(\frac{\partial R}{R} - 2\frac{\partial R_t}{R_0}\right)$$
$$-2\int_{-x_0}^{x} i_1\left(1 + \frac{\partial R_t}{R}\right)\left(1 + \frac{\partial R_t}{R_0}\right)\left[\int_0^x j\,dx\right]dx, \quad . \quad (4)$$

where

∂H = rate of loss of heat ;

∂R_t = change in resistance of the filament due to turning on the thermionic current;

R = the resistance of the filament ;

R_0 = the resistance of the circuit of battery B ;

j = the thermionic current flowing into unit length of the filament ;

x_0, x = coordinates along the filament measured from the centre of distribution of the thermionic current ;

ρ = the resistance per unit length of the filament with T off ;

T = the thermionic current.

The other symbols have the same significance as in (2) and (3). Expression (4) divided by expression (2), the change in the rate of supply of energy due to shunting x with y, gives the value of the ratio $\partial \dot{H}/\partial \dot{E}$, which is equal to $\partial R_t/\partial R_e$, or,

$$\frac{\partial \dot{H}}{\partial \dot{E}} = \frac{\partial R_t}{\partial R_e} = \frac{D_T - p\psi}{D_e}, \quad \ldots \ldots (5)$$

where $p\psi$ is the deflexion of the galvanometer due to the uncompensated part of the disturbance produced by the thermionic current in the bridge circuit. Expressions similar to (4) and (5) are obtained for the bridge current reversed, except that $-i$ is substituted for $+i$, and $-p\psi$ for $+p\psi$. Substituting (4) in (5) for the two cases, adding, and simplifying, the expression for the cooling effect is obtained in the form

$$\phi + \frac{\alpha}{e}(\theta_1 - \theta_0) = \frac{2(1-2q)i_1^3(D_T + D_{T'})Rx^2}{(T + T')D_e V(x+y)}\left(1 + \frac{x+y}{x^2}\right)\partial R_e, \quad (6)$$
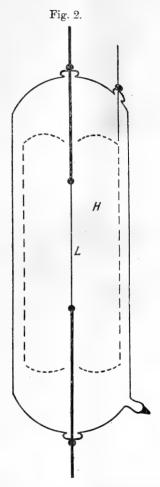
where the primed letters refer to the values with current reversed, and ∂R_e is given by (3).

Mounting and Preparation of Filaments.

The filaments were mounted axially in glass tubes as illustrated in fig. 2. The tungsten and tantalum filaments were welded to copper leads, which were in turn welded to stout platinum leads that were sealed into the ends of the tubes. The molybdenum was silver-soldered to the copper leads, and the carbon was attached by means of a paste which was supplied for the purpose by the Edison Electric Lamp Company of Harrison, New Jersey. The anode was made from clean copper gauze bent into a cylinder to fit the glass tube

and crimped over at the ends so as almost completely to enclose the filament. Outside connexion was made through a platinum wire sealed into the glass.

Fig. 2.

L = filament; H = copper gauze anode.

After a filament was mounted as described the tube was attached to a rotary mercury-pump and enclosed in a vacuum furnace. During exhaustion the furnace was maintained at a temperature of about 600 degrees centigrade. When the McLeod gauge showed a pressure of about 1×10^{-4} mm. of mercury, the furnace was turned off, connexion with the

pump was broken and exhaustion was completed with charcoal and liquid air. Liquid air was also placed on a trap near the furnace so as to prevent mercury vapour and other condensible gases from diffusing back into the tube. As soon as it had cooled sufficiently the furnace was opened and the filament was glowed out at a temperature near its melting-point. This process was accompanied by a considerable evolution of gas. This evolution did not continue long, so that after about fifteen or twenty minutes the pressure decreased to about 2×10^{-5} mm., in most cases with the wire hot. The tubes were now sealed off and were ready for use. In one case readings were taken on a tungsten filament before sealing off.

The above procedure was not followed with carbon except in one case where the tube was sealed off when the pressure was down to 1×10^{-4} mm. with the wire hot. It was found that the carbon gave up a very great quantity of occluded gas. It seemed impossible to glow it out to a point where no more gas was given up. For reasons that will be discussed later it is thought that no serious error arose from the lack of ideal conditions in the case of carbon.

The temperature of the filaments, except in the case of tungsten, were estimated by comparing the colour of the filament with that of a tungsten filament for which a temperature-current curve was available. The tungsten temperatures were given by the curve referred to above, for which thanks are due to Dr. Irving Langmuir, of the General Electric Company Research Laboratory. Dr. Langmuir was kind enough to furnish most of the filaments used in this research.

The tungsten and tantalum filaments were fine drawn wires similar to those used in the construction of metallic filament lamps. The molybdenum was in the form of a fine wire about ·1 mm. in diameter. The carbon filaments were taken from burned-out carbon lamps of the " metalized " filament type. The filaments of these lamps are baked out in the process of manufacture at a temperature of 3000° C., thus changing most of the carbon to graphite and greatly purifying the material. The other materials were regarded as pure, though no investigation was made except that a test on tungsten showed no trace of thorium.

The values of ϕ are given below in the form adopted by Cooke and Richardson. In their work they neglected the factor $1/i$ in the expression for ∂R_e. This omission did not materially affect their values for tungsten, but it is very important for many of the values found here.

CARBON.—Filament #1.

θ.	i.	D_{e}.	D_{T}.	R.	$T \times 10^{6}$	V.	Fil. sh. $\phi + \frac{a}{e}(\Delta\theta).$*	St. sh. $\phi + \frac{a}{e}(\Delta\theta).$	$\frac{a}{e}(\Delta\theta).$	ϕ.
Approx. 1650	·770	38·8	8·8	7·912	75·6	24·7	......	4·948	·231	4·72
	·770	39·8	1·55	7·918	74·9	24·7				
	·775	4·23	1·3	8·000	122·5	30·4				
	·775	5·5	1·0	8·004	122	30·5	4·54	......	·231	4·31
1700	·800	40·4	8·7	7·927	132	24·7	5·116	......	·240	4·88
	·800	41·3	7·8	7·933	132	24·7				
	·800	39·7	2·5	7·976	136	24·7	......	5·034	·240	4·79
	·800	40·8	13·9	7·970	136	24·7				
1750	·835	5·1	1·7	8·249	289	30·4	4·3886	......	·248	4·140
	·835	4·5	2·2	8·242	285	30·4				
	·835	5·3	3·8	8·250	280	30·4	......	4·6683	·248	4·420
	·835	4·9	·5	8·256	278	30·4				
1800	·890	7·0	3·6	8·211	700	24·7	4·750	......	·256	4·50
	·890	6·6	5·3	8·206	705	24·7				
	·890	7·1	8·9	8·290	780	24·7	......	4·676	·256	4·42
	·890	6·7	2·3	8·291	810	24·7				
	·900	50·0	3·6	8·189	651	24·8	5·164	......	·264	4·90
	·900	52·1	3·3	8·196	649	24·8				
	·900	52·3	5·2	8·278	631	24·8	......	4·637	·264	4·38
	·900	51·8	1·1	8·284	666	24·8				
1850	·900	51·0	23·7	8·194	610	24·8	4·647	......	·264	4·37
	·900	52·7	34·9	8·189	611	24·8				
	·900	5·5	5·0	8 426	832·6	30·5	4·902	......	·264	4·64
	·900	4·9	5·8	8·420	835	30·5				
	·900	5·9	9·8	8·429	815	30·5	......	4·799	·264	4·54
	900	5·3	1·4	8·433	825	30·5				

Mean .... 4·500

Filament #2.

θ	i.	D_{e}.	D_{T}.	R.	$T \times 10^{6}$	V.	Fil. sh. $\phi + \frac{a}{e}(\Delta\theta).$*	St. sh. $\phi + \frac{a}{e}(\Delta\theta).$	$\frac{a}{e}(\Delta\theta).$	ϕ.
Estimated. 1800	1·49	21·34	11·65	4·037	713	29·7	4·878	......	·256	4·61
	1·49	21·46	4·93	4·034	685	29·7				
	1·49	20·78	7·90	3·997	658	29·7	......	5·214	·256	4·96
	1·49	20·51	8·48	4·002	670	29 7				
1900	1·62	23·2	36·0	4·095	3085	30·2				
	1·62	21·2	14·9	4·095	2063	30·2	......	4·43	·272	4·16
1820	1·50	22·02	5·0	4·033	738	29·7				
	1·50	21·66	13·08	4·035	775	29·7	5·018	......	·26	4·76

Mean .... 4·62

* $\Delta\theta$ represents $(\theta_{1} - \theta_{0})$.

CARBON (*continued*).—Filament ♯3.   (Alternating current method.)

θ.	i.	D_e.	D_T.	R.	$T \times 10^{-6}$.	V.	Fil. sh. $\phi + \frac{a}{e}(\Delta\theta)$.	St. sh. $\phi + \frac{a}{e}(\Delta\theta)$.	$\frac{a}{e}(\Delta\theta)$.	ϕ.
	·698	34	33·8	4·521	1605	36			·301	4·93
2000	·698	35·2	33·3	4·510	1635	36		5·231		
	·700	36·5	59·8	4·510	1613	36				
	·700	34·6	10	4·539	1600	36	4·442		·301	4·14

<div align="right">Mean .... 4·53</div>

Filament ♯4.—After exhaustion in vacuum furnace.

θ.	i.	D_e.	D_T.	R.	$T \times 10^{-6}$.	V.	Fil. sh. $\phi + \frac{a}{e}(\Delta\theta)$.	St. sh. $\phi + \frac{a}{e}(\Delta\theta)$.	$\frac{a}{e}(\Delta\theta)$.	ϕ.
	·882	6·8	5·48	8·441	660	24		5·2072	·240	4·97
1700	·882	6·7	4·2	8·441	630	24				
	·882	6·7	2·75	8·527	692	24	4·936		·240	4·70
	·882	6·8	6·97	8·527	700	24				
	·895	6·8	5·6	8·398	565	24		4·621	·24	4·38
1740	·895	6·8	1·6	8·398	555	24				
	·895	6·8	3·03	8·309	521	24	4·667		·24	4·43
	·898	6·5	3·56	8·317	510	24				
1900	·934	7·25	7·25	8·511	1012	24		5·104	·27	4·83
	·934	7·25	6·19	8·518	1022	24				

<div align="right">Mean .... 4·66
Mean of all values .... 4·55</div>

Value of "b" corresponding to $4\cdot55 = 52800$.

MOLYBDENUM.

θ.	i.	D_e.	D_T.	R.	$T \times 10^{-6}$.	V.	Fil. sh. $\phi + \frac{a}{e}(\Delta\theta)$.	St. sh. $\phi + \frac{a}{e}(\Delta\theta)$.	$\frac{a}{e}(\Delta\theta)$.	ϕ.
	1·410	34·2	14·6	1·263	282	24	4·870		·248	4·622
1750	1·410	34·4	17·3	1·259	278·5	24				
	1·410	34·8	20·2	1·259	279·5	24				
	1·410	34·2	11·9	1·263	279·2	24		4·846	·248	4·598
	1·500	38·2	33·5	1·290	563·5	24		4·943	·264	4·679
1850	1·500	38·0	25·25	1·291	562·5	24				
	1·500	38·3	36·9	1·285	557·5	24				
	1·500	37·9	19·9	1·290	557·5	24	4·862	.. ...	·264	4·598
	1·545	39·9	33·2	1·331	1014·5	24	4·848		·274	4·574
1900	1·545	40·1	65·9	1·331	1070	24				
	1·550	40·4	58·0	1·331	1050	24				
	1·550	40·6	42·0	1·336	1072·5	24		4·863	·274	4·580
	1·575	42·0	69·9	1·326	1150	23·5			·281	4·580
1975	1·575	42·3	36·4	1·328	1150	23·5	4·861			
	1·575	41·3	43·75	1·329	1160	23·5				
	1·575	43·1	64·5	1·329	1188	23·5		4·745	·281	4·464

<div align="right">Mean .... 4·588</div>

<div align="right">"b" = 53200.</div>

TANTALUM.

θ.	i.	D_e.	D_T.	R.	$T \times 10^{-6}$.	V.	$\phi + \frac{a}{e}(\theta_1 - \theta_0)$. Fil. sh.	St. sh.	$\frac{a}{e}(\Delta\theta)$.	ϕ.
1700	·605	4·05	2·03	4·438	69·07	24·5	4·974	......	·240	4·734
	·605	4·23	1·43	4·434	65·7	24·5				
	·605	4·00	2·01	4·436	64	24·5	......	4·579	·240	4·519
	·605	4·18	1·12	4·443	64·4	24·5				
1750	·639	5·57	5·29	4·365	313·5	24	4·703	......	·248	4·455
	·639	5·05	11·30	4·356	316	24				
	·639	5·04	8·45	4·351	321	24	......	4·782	·248	4·534
	·639	5·04	8·32	4·372	325	24				
1775	·648	5·12	18·97	4·401	545	24	4·590	......	·250	4·340
	·648	5·37	8·25	4·411	535·5	24				
1800	·660	5·13	10·33	4·514	402·5	24·1	4·984	......	·256	4·723
	·660	5·00	8·42	4·520	392·5	24·1				
	·660	5·01	11·29	4·522	393·5	24·3	......	4·644	·256	4·383
	·660	4·97	5·495	4·522	378·5	24·3				
	·662	5·55	13·02	4·430	495·5	24	......	4·791	·257	4·534
	·662	5·33	11·44	4·440	504·5	24				
1850	·688	5·42	24·84	4·582	742·35	24·3	4·758	......	·264	4·494
	·688	5·61	7·10	4·579	744·1	24·3				
	·688	5·36	14·36	4·572	750·6	24·3	......	4·796	·264	4·532
	·688	5·41	17·73	4·581	766·5	24·3				
1900	·713	6·63	25·36	4·597	1715	24·3	4·845	......	·274	4·571
	·713	5·74	49·42	4·620	1712	24·2				
	·713	5·22	38·18	4·601	1660	24·2	......	4·582	·274	4·308
	·715	7·97	35·51	4·600	1912	24·2				

Mean .... 4·511

" b " $= 52500$

TUNGSTEN.

Wire ♯ 1.   (After thoroughly ageing out.)

θ.	i.	D_e.	D_T.	R.	$T \times 10^{-6}$.	V.	Fil. sh. $\phi + \frac{\alpha}{e}(\Delta\theta)$.	St. sh. $\phi + \frac{\alpha}{e}(\Delta\theta)$.	$\frac{\alpha}{e}\Delta\theta)$.	ϕ.
2060	·321	17·6	123·9	19·815	588	24·5	4·8499	......	·301	4·547
	·321	17·5	55·39	19·815	615	24·5				
	·320	17·7	142·62	20·219	615	24·5	......	4·7635	·301	4·462
	·321	18·1	49·05	20·208	690	24·5				
	·320	16·9	116·6	20·020	570	24·2	4·7797	......	·301	4·479
	·320	16·9	56·3	20·063	582	24·2				

Wire ♯ 2.

θ.	i.	D_e.	D_T.	R.	$T \times 10^{-6}$.	V.	Fil. sh.	St. sh.	$\frac{\alpha}{e}\Delta\theta)$.	ϕ.
2000	·294	29·8	27·4	19·180	90	10·3	......	4·550	·290	4·260
	·294	29·4	25·64	19·18u	91	10·3				
	·295	29·94	21·2	19·00	94·5	10·3	4·480	......	·290	4·190
	·295	30·2	29·82	19·00	94·5	10·3				
	·295	28·92	28·8	19·070	92·5	10·3	4·8423	......	·290	4·552
	·295	29·08	2i·38	19·070	88	10·3				
	·293	28·94	25·90	19·425	92·5	10·3	......	4·6887	·290	4·399
	·293	28·94	26·50	19·425	102·5	10·3				

Wire ♯ 3.

θ.	i.	D_e.	D_T.	R.	$T \times 10^{-6}$.	V.	Fil. sh.	St. sh.	$\frac{\alpha}{e}\Delta\theta)$.	ϕ.
2050	·303	11·59	5·67	12·534	61	24	4·511	......	·300	4·211
	·303	11·64	15·72	12·531	61	24				
2150	·333	13·7	51·03	13·559	291	24	......	4·858	·316	4·542
	·333	13 8	39·49	13 559	291	24				
	·333	13·98	39·26	13·555	286	24	4·786	......	·316	4·470
	·333	14·2	50·33	13·555	286	24				
2200	·352	15·61	103·56	14·167	663	24	4·9224	......	·324	4·598
	·351	15·62	90·59	14·163	663	24				
	·351	15·75	21·67	14·400	721	24	......	4·9575	·324	4·633
	·351	15·38	185·88	14·400	715	24				
2010	·300	19·35	5·79	12·681	65	12·22	4·7840	......	·290	4·494
	·300	20·19	15 54	12·684	66	12·22				
	·300	20·01	10·54	12·497	61	12·22	......	4·869	·290	4·579
	·300	20·1	10·17	12·496	61	12·22				
2150	·336	23·8	47·7	13·672	359	12·12	......		·316	
	·336	24·8	48·9	13·673	360	12·12	4·8607	......	......	4·545
	·386	24·2	70·6	13·884	386	12·12				
	·336	24·5	32·3	13·883	385	12·12	......	4·9222	·316	4·606
2150	·335	24·42	32·74	13·872	371	12·11	5·040	......	·316	4·724
	·335	4·04	71·24	13·872	375	12·11				
	·336	25·20	49·49	13·661	350	12·11	......	4·670	·316	4·354
	·336	25·79	48·62	13·662	352	12·11				

Mean .... 4·478

It is difficult to make any definite statement as to the exact accuracy of the above measurements because of some apparently unavoidable errors. In the cases of tungsten and tantalum the galvanometer was subject to slow drifts, sometimes in one direction and sometimes in the other. It is thought that these drifts were caused by a lack of homogeneity in the filaments. A tungsten filament when passed between steel rolls broke up into five or six finer filaments. It may be that these wires are never quite homogeneous. It is thought that errors of this sort are largely eliminated from the mean. For tungsten the mean variation from the mean of the eighteen values found was ·11 volt or 2 per cent. It is thought that this represents about the accuracy for the tungsten and tantalum measurements. Owing to the lack of ideal conditions for carbon and to the fact that the small temperature-resistance coefficient caused the galvanometer deflexions to be small, the carbon values are probably not accurate within less than 4 per cent. Only one specimen of molybdenum was examined. The readings were good, however, and may be regarded as accurate within the same limits as the values for carbon.

It is interesting to note in this connexion that values of ϕ found for one wire that was known to be not homogeneous were more nearly normal than were corresponding values of "b" found by observing the temperatures and currents. From this observation it was concluded that measurement of the value of ϕ is less subject to error than are corresponding measurements of the value of "b." It may be that the value of b can be more accurately determined from the cooling effect than it can be from the current-temperature relationship.

III. Certain Features related to the Problem.

1. *Identification of b with ϕ.*

It will be remembered that in the theoretical derivation of the Richardson equation, b is supposed to represent the work done when an electron escapes from the surface. Since this work is measured by the potential difference represented by ϕ, it follows that b and ϕ should be equivalent if the assumption in regard to b is correct.

The relationship between ϕ and b should be given by

$$b = \frac{\phi e}{R}, \quad \ldots \quad \ldots \quad (7)$$

where e is the charge on an electron and R is the gas constant calculated for a single molecule.

It is important that the equivalence of ϕ and b be established in order that the validity of the Richardson equation should be more completely demonstrated, and also for another reason. The assumption involved in b rests upon the further assumption that the translational kinetic energy of an electron in a hot metal is equal to the energy of a gas molecule in a gas at the same temperature as the hot metal. This latter supposition has been proved true by the experiments of Richardson and Brown [*]. Their work receives additional support if it is demonstrated that ϕ and b measured independently are shown to be equivalent. The term $\frac{\alpha}{e}(\theta_1 - \theta_0)$ in the expression for ϕ is based upon the results of Richardson and Brown's work. However, as pointed out elsewhere, this term contributes but little to the value of ϕ, so that its presence does not seriously affect the validity of the check.

The experimental verification of equation (7) was attempted by Richardson and Cooke, but, as explained above, their values of ϕ obtained from the heating effect were of insufficient accuracy to give more than an approximate test. Their work on tungsten, however, was carried out under ideal conditions and by a method that is capable of giving accurate results. They found for tungsten

$$\phi = 4 \cdot 24 \text{ eq. volts,}$$

from which, by eq. (7)

$$b = 49400.$$

Langmuir [†] has determined b very accurately for the same metal, and has found

$$b = 52500.$$

Recent work in this laboratory by Dr. K. K. Smith [‡] gives

$$b = 54700.$$

Dr. Smith's value was obtained as the mean of a large number of determinations in which high and low values are given equal weight. It is probable that the low values are more nearly correct. If Langmuir's value is given weight 2 and Smith's weight 1, then the weighted mean of the two determinations gives

$$b = 53600.$$

The Cooke and Richardson value as calculated from ϕ differs

* Phil. Mag. vol. xvi. p. 353 (1908).
† Phys. Rev. Dec. 1913; *Phys. Zeit.* vol. xv. p. 516 (1914).
‡ Phil. Mag. June 1915.

from this by nearly 7 per cent. It seemed to the writer that this discrepancy was great enough to leave a reasonable doubt as to the exact equivalence of b and ϕ.

On account of the importance of the relationship it seemed advisable to obtain more specific information on this point. The present measurements on tungsten were taken with this end in view. Tungsten was selected for the purpose because it is the only metal for which extensive measurements have been made under ideal conditions to determine the value of b. Cooke and Richardson investigated only one specimen in their measurement of the cooling effect. It was thought possible that an extended investigation might yield results more in harmony with the published values of b. The mean of the eighteen values found for tungsten gives

$$\phi = 4 \cdot 478,$$

from which

$$b = 52130.$$

This value is within ·7 per cent. of Langmuir's, and differs from the weighted mean of Langmuir's and Smith's value by 1·6 per cent. Each of these differences is well within the limits of accuracy of the present experiments.

The above result leaves little doubt as to the exact equivalence of ϕ and b within the limits of accuracy of the above determinations, and consequently justifies the assumption in regard to b involved in the Richardson equation, and lends additional support to the findings of Richardson and Brown concerning the kinetic energy of electrons.

2. *Effect of Gases on the Value of* ϕ.

Langmuir has shown that residual gases strongly influence the value of b. It seemed worth while to test for corresponding effects in the value of ϕ. Osmium when heated gives out gas copiously. An osmium filament mounted and treated in the usual manner but not completely glowed out, would give up gases that are probably free from water-vapour. These gases react with the hot cathode to form compounds which condense on the walls of the tube, so that there is a gradual improvement in the vacuum, a gas-free state being finally arrived at. A tube so treated gave initially for the cooling effect 5·93, after a few hours heating the value was 5·16. The filament burned out before the gases were all consumed, so that the final value was not obtained. A tungsten filament similarly treated but not at first sealed off from the charcoal tube gave values as

follows :—Before sealing off, 5·799 ; immediately after seal-
ing off, 5·872. Succeeding values taken at various intervals
for two or three hours were 5·44, 5·399, 5·270, 5·116, 4·79,
4·85. The subsequent values oscillated around 4·8. Carbon
behaved similarly to the osmium and tungsten in that the
initial values were high and the later values were lower and
constant. A series of readings to determine the variation
of ϕ with time was not taken ; it was noticed, however, that
it took carbon much longer to become " normal " than it
did tungsten. Usually the carbon filaments were heated
from twenty-four to forty-eight hours before readings were
recorded.

Langmuir investigated the reduction of the residual gases
in the presence of a hot wire, and termed the phenomenon
the " clean-up effect " [*]. It is evident that in the progress
of the clean up the vacuum was cleared of all active gases
and successively lower pressures were produced. We have
seen that successively lower values of ϕ were also obtained.
The value found for tungsten in the unsealed tube is what
was expected as the initial value immediately after sealing
off. It is noticed that the latter value was greater than the
former. This discrepancy was undoubtedly due to the fact
that certain gases were liberated from the portion of the
glass that was heated during the sealing-off process. It
was concluded from the behaviour of osmium and tungsten
that residual gases affect the value of ϕ in precisely the
same way that they affect the value of b. This result was
expected.

The behaviour of carbon is interesting. It may be re-
membered that except in one case the carbon filaments were
not subjected to the vacuum-furnace treatment. There
were no waxed or ground-glass joints, except one that con-
nected the glass tubing to the pump, and the pump was kept
running continuously. Since there could be no addition
of gas to the experimental chamber, it was thought that
after sufficient time a condition would be reached in which
the active gases would be consumed and the carbon would
be surrounded only by residual gases inert to carbon. If
the variation in ϕ is due to the influence of active gases,
then the elimination of these ought to produce the same con-
stancy of behaviour in regard to the cooling effect as the
elimination of gases by the clean-up effect. In fact the
clean-up effect removes only the active gases. The results
of the carbon showed practically the same behaviour as was

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[*] Journ. Amer. Chem. Soc. vol. xxxiv. p. 1310 (1912).

obtained with tungsten and osmium. The pressure in the tube during the carbon experiments varied from 1×10^{-4} mm. with the wire hot to 3×10^{-5} mm. with the wire cold, approximately. This behaviour of carbon verifies for the value of ϕ, found when inert gases are known to be present, an observation that Langmuir made on tungsten. He found that the presence of argon in the experimental tube did not affect the value of b. Argon is inert to tungsten. It would be interesting to find out if any pressure of inert gas would affect the value of ϕ. This was not attempted in the present investigation.

3. *Nature of Surface Films.*

It is probable that active gases affect the value of ϕ through the formation of surface films. It is interesting and important to consider the nature of these films. The work of Richardson and Cooke shows that the heating effect measured under conditions that are not ideal is greater than the cooling effect measured under ideal conditions. It is probable that the heating effect, like the cooling effect, is increased in the presence of active residual gases. If the film acts merely as a high resistance through which the escaping electron must go, then the work that an electron does in escaping would be exactly represented by an equivalent Joule heating effect. Since we may regard the film as at all times in thermal equilibrium with the hot surface, this Joule heating would act to decrease the cooling due to the escape of electrons, and we should expect the cooling effect to be decreased by the film. This is, however, contrary to observation. The alternative view is to regard the film as charged. A charged film might be produced by the ionization of surface molecules of a surface compound and the loss of electrons to the interior of the metal, or the arrangement of ions into a double layer with positive ions on the outside. The field within such a film would oppose the passage of escaping electrons and accelerate the passage of entering electrons. Since both the heating and cooling effects are increased, there must be some such field acting at each surface. There is reason to expect such an arrangement of double layers at a metallic surface. The same force which retains electrons within a metallic surface would also tend to retain negative ions within that indefinite region called the "surface." Positive ions would gravitate to the outer portion of the region occupied by the ions and molecules that make up the so-called film.

4. *Contact Potentials.*

Richardson has developed a relation for contact potentials in the form

$$eV_c = W_1 - W_2 + \psi,$$

where V^c represents contact potential, e the charge on an electron, W_1 and W_2 work done on an electron in leaving and entering the metallic surfaces, and ψ a term of the order of the Peltier effect.

This expression may be written in terms of ϕ as

$$V_c = \phi_1 - \phi_2, \quad \ldots \ldots \quad (8)$$

where the Peltier term is neglected. This expression gives the contact potential as the difference of the ϕ's for the two metals; so that to test the much discussed question as to the existence of intrinsic potentials, it is only necessary to measure ϕ for a series of metals and substitute in equation (8). Measurements of ϕ for metals far enough apart in the voltaic series to test the above equation have not been made with sufficient accuracy for the purpose. However, Richardson noticed that the values of the heating effect for the metals examined by Richardson and Cooke lay close together. In explaining this seeming coincidence, he suggested, as stated above, that the heating effect is connected with the cooling effect through the relation

$$\phi_1 = \phi_2 + V_c. \quad \ldots \ldots \quad (9)$$

He recognized that the non-existence of contact potentials would explain the results as well.

It has been shown that the observations on iron cannot be taken to support the relationship as he expressed it. Moreover, it was shown that the heating effects measured by Cooke and Richardson did not equal the cooling effect of the hot emitter as measured by the same experimenters, although the theory demanded that they should, since the effect measured as the heating effect was supposed to be $(\phi_2 + V_c)$. The ϕ's so far determined from the cooling effect have been identical within their limits of accuracy, so that between the metals for which this effect has been measured, no contact potential exists as great as two-tenths of a volt.

It was observed that quite different values of ϕ were obtained when active residual gases were present. For this case there would ordinarily be differences in the ϕ's for different metals, and the differences would be of an order of magnitude sufficient to account for contact potentials.

This condition prevailed in the Richardson and Cooke experiments. The question immediately arises, Why did equation (9) not hold for their values? A seemingly reasonable explanation may be offered, as follows :—It has been shown that the presence of active gases always tends to increase ϕ. Also that inert gases do not affect ϕ. The low value they found for the cooling effect for osmium would indicate that the gases active with osmium had been mostly consumed, so that the cooling effect measured must have been that peculiar to the material under ideal conditions. If the true value of ϕ for the two metals was the same, then the ϕ actually existing for the cold metal must have been larger than that for the osmium under the conditions of the experiment. If this were true, then the order of the metals in the voltaic series was reversed, and equation (9) should have been written

$$\phi_1 = \phi_2 - V_c,$$

which would make the heating effect greater than the cooling effect by an amount comparable with the order of magnitude of the contact potential difference. The observed difference was $1\cdot5$ volts. This is of the required order of magnitude. Since there was no counterbalancing film at the osmium surface, this potential difference is greater than would ordinarily exist.

5. *A Method for Measuring Temperatures of Filaments.*

The thermionic current is an exponential function of the temperature. Owing to the rapid variation of the current with the temperature, it ought to be possible to measure high temperatures very accurately by observing the thermionic currents, since these may be determined very accurately *. The method has not been employed, partly because the emission properties of hot surfaces have not been found to be constant. There has been a further difficulty in the fact that independent temperature determinations have been necessary to determine the current-temperature curve for any wire. The work of Langmuir, and more recently that of Smith, have shown that under ideal conditions the emission properties of hot bodies are constant. The difficulty in regard to calibration may be obviated if b in the current-temperature equation is determined by measuring ϕ.

* *Cf.* O. W. Richardson, Phys. Rev, vol. xxvii. p. 183 (1908).

There is a temperature term in the expression for ϕ, viz. $\frac{a}{e}(\theta_1 - \theta_0)$; but this term contributes at most only about 7 per cent. to the value of ϕ.

If the Richardson equation be written in the form

$$\log i - \frac{1}{2}\log\theta = -b \cdot \frac{1}{\theta} + \mathrm{A},$$

or

$$\mathrm{X} = -b\mathrm{Y} + \mathrm{A},$$

where

$$\mathrm{X} = \log i - \frac{1}{2}\log\theta \quad\text{and}\quad \mathrm{Y} = \frac{1}{\theta},$$

then the current-temperature curve becomes a straight line whose slope is $-b$. Knowing ϕ, b may be obtained from equation (7). A single determination of i for a known temperature will fix the position of the line. Such a determination may be made by observing i for a known temperature, say the melting-point of platinum. The curve once fixed may be used to determine higher temperatures. The method would give relative temperatures with great accuracy, and would give absolute values with an accuracy depending upon the accuracy of the determination of the melting-point of platinum. It has the advantage that it is independent of radiation formulæ. If, as seems probable, ϕ is very nearly constant for all metals, it would not be necessary to determine ϕ in applying the method. In regard to the constancy of ϕ, it may be pointed out that all the determinations of the cooling effect so far made have given identical values of ϕ within the limits of experimental error. However, the metals tested have been at one end of the voltaic series where large differences would not be expected. Richardson and Cooke determined ϕ from the heating effect for much more electro-positive metals. Their measurements were not accurate, but the values found were greater than, instead of less than, the values found for ϕ from the cooling effect. It has been pointed out that their measurements probably contained an error, due to the ionized film at the cold surface. If suitable allowance be made for this error, the values found for ϕ for these metals fall in with the values found from the heating effect at about 4·5 volts. The point is important, and will be investigated further.

Summary.

1. Richardson and Cooke's work on the heating effect has been reviewed, and certain details of relatively secondary importance have been criticised, viz.:—

(*a*) The conditions of their experiments were not ideal in the light of later information, and their results are not accurate as regards values of ϕ for the metals tested.

(*b*) Their experiments on the effects of gas pressure are inconclusive, since they did not get rid of the residual gases, and since the big effects of gases are known to disappear only with the last traces of the residual gases.

(*c*) The relationship between the heating and cooling effects, as tested by Richardson, is shown to be inconsistent with the facts of their experiments. Another relationship applicable to the conditions of their experiments is suggested.

2. Values of ϕ for three new materials are given and new values are offered for tungsten.

3. The complete identification of b with ϕ is established, and additional evidence is shown in support of Richardson and Brown's experiments on the kinetic energies of electrons.

4. It is shown that traces of active gases influence ϕ in the same way that they influence b, and that traces of inert gases do not affect the value of ϕ.

5. It is shown that surface-films formed under the influence of active gases must be ionized, and that the field produced opposes the escape of electrons. The field due to the film is apparently independent of the field due to the applied potentials.

6. Evidence is offered that intrinsic potential differences do not exist, but that observed contact effects may be attributed to the influence of ionized films.

7. A new method for determining filament temperatures is described in which the Richardson equation is used and b is determined from measurements on ϕ.

XXX. *Note on the Scattering of X-rays and Atomic Structure.*
By C. G. Barkla, *F.R.S., Professor of Natural Philosophy,*
and Janette G. Dunlop, *M.A., B.Sc., Carnegie Research*
Scholar, University of Edinburgh *.

THE results of experiments made by one of the writers
on the radiation proceeding from substances containing
only light elements when these were exposed to Röntgen
radiation led to the conclusion that this radiation, as observed
under ordinary experimental conditions, was almost purely a
scattered X-radiation and that the scattering particles were
not the ions or atoms, but the constituent electrons †. It
was shown that the intensity of the scattered radiation over
a wide range of penetrating powers was approximately
independent of the penetrating power of the radiation
scattered; and, with the possible exception of hydrogen
among the light elements, the intensity was proportional
merely to the quantity‡ and independent of the quality of
matter traversed by the primary radiation.

From measurements of the intensity of Röntgen radiation
scattered from light elements, applied to the theory as given
by Sir J. J. Thomson, the number of electrons in the atom
was determined. With the data for e/m and e for an electron
at that time available, it appeared to be several times the
atomic weight of the element considered. Applying the
more recently determined values of e/m, e, and n—the number
of molecules per c.c. of gas—to the same measurement, the
number of electrons was later § found to be almost exactly
half the atomic weight, for elements of atomic weight
greater than that of hydrogen and not greater than that of
sulphur ||. This determination accounted for the previously
observed anomalous behaviour of hydrogen, for only if
hydrogen had possessed one electron for each *pair* of atoms
could it have scattered only as much mass for mass as any
other light element. Hydrogen had been found to scatter a
little more than twice as much, mass for mass, as the other

* Communicated by the Authors.
† Barkla, Phil. Mag. June 1903, May 1904, and later papers.
‡ Measured by mass.
§ Barkla, Phil. Mag. May 1911.
|| Sir E. Rutherford about the same time (Phil. Mag. May 1911)
arrived at the complementary conclusion: that the central (positive)
charge of an atom is about half the atomic weight times the charge of
an electron.

light elements*; Crowther† later found something a little less than twice as much. This higher value simply meant that the number of electrons in the hydrogen atom was *equal to* the atomic weight. The anomalous behaviour of hydrogen is thus strong evidence of the applicability of the theory.

Measurements of the scattering from elements of higher atomic weight than sulphur, however, led to a different experimental conclusion; for copper was found to scatter about twice as much and silver about six times as much as an equal mass of one of the light elements‡. This result was in general confirmed by the later experiments of Crowther §. In Table I. are given the relative values of the energy scattered from equal masses of eleven elements.

TABLE I.

Showing relative intensities of the X-radiation scattered from equal masses of various elements.

Element.	Atomic Weight.	Relative energy scattered. (Barkla.)	Relative energy scattered. (Crowther.)
H	1	2·4 ?	1·7
He	4	...	1·1
C...............	12	1·0	1·0
N	14	1·0	1·0
O	16	1·0	1·0
Al	27	...	1·05
S...............	32	1·0	1·4
Ni	59	...	3·5
Cu	63·5	2·0‖	3·5
Ag	108	6·5‖	...
Sn	118	...	5·5

‖ Barkla & Sadler.

If we applied the theory unmodified to each of these results, we should conclude that

(1) A hydrogen atom possesses one scattering electron;
(2) An atom of helium, carbon, nitrogen, oxygen, aluminium, or sulphur possesses $w/2$ electrons approximately;
(3) An atom of nickel, copper, silver, or tin possesses w to $3w$ electrons;

where w is the atomic weight of the element.

* It was thought at the time that the discrepancy was due to impurity of the hydrogen. Crowther's determination indicated that this was not the case.

† Phil. Mag. Nov. 1907.

‡ Barkla & Sadler, Proc. Lond. Phys. Soc. June 1908; and Phil. Mag. Oct. 1908.　　　　　§ Proc. Camb. Phil. Soc. May 1911.

The first two conclusions find support from other reasoning, and are becoming generally accepted. There is, however, no evidence in support of the tentative conclusion regarding the heavier elements. Indeed, we have never considered the validity of the theory as applied to these elements to have been established ; for the results were based upon isolated observations which did not show that the necessary conditions were fulfilled. It seemed possible that the simple theory of scattering was not applicable to the passage of radiation of the particular wave-length used in these experiments through the heavier elements. It was therefore decided to study the effect of a considerable variation of wave-length on the scattering. The following investigation was undertaken in order to obtain further experimental data on the subject.

There is much greater experimental difficulty in determining the scattering from these heavier elements than from the lighter, because under ordinary experimental conditions the scattered radiation from each of the heavier is accompanied by a much more intense fluorescent (characteristic) X-radiation which is liable to mask the true scattering effect. The idea of using homogeneous beams of X-rays as primary radiations was soon abandoned, as after the elimination of all fluorescent X-radiation for the complex secondary set up, the intensity of the purely scattered radiation was too small to measure with any accuracy. Instead of this, a primary beam from an X-ray tube was used under conditions which limited the range of wave-length employed. The beam of radiation was one giving a continuous spectrum between narrow limits of wave-length,—at least the effective portion of the beam was that between such limits.

Two methods were employed in examining the radiation scattered from copper, silver, tin, and lead.

Method (a).

In one, the scattered radiation from a thin sheet of substance was compared with that from a thin sheet of aluminium subsequently placed in the same position in the primary beam. The intensity of the primary beam was standardized by one electroscope and that of the scattered radiation measured in a second electroscope. After correction for the absorption of the primary and scattered radiations in these scattering sheets—corrections which in this case were not large,—the relative intensities of radiation scattered in a direction perpendicular to that of propagation of the primary radiation from equal masses of, say, copper and aluminium

were easily determined. (The corrections necessary for absorption were obtained from subsidiary absorption experiments.)

The reason for the choice of this particular direction for the scattered radiation measured is simply that it in all probability gives us the truest measure of the whole energy of radiation scattered. An " extra radiation " *, the bulk of which is included within a cone of small angle in the forward direction, is not included in the scattered radiation measured in these experiments, for this extra radiation cannot be explained on the simple theory of scattering, and in all probability is due to processes other than those considered.

Method (b).

In the second method thick sheets of scattering substance were used, so thick as to transmit no appreciable portion of the primary radiation. The intensity of scattered radiation appearing through the face of incidence of the primary X-radiation was compared for various scattering substances placed successively in the same position. Measurement and standardization were effected as before. It is easily shown that the effective thicknesses of material from which the radiations emerge are inversely proportional to the coefficients of absorption (λ) in the various substances of the radiation used, provided that radiation is homogeneous. Thus with primary rays normal to the surface, the intensity of primary radiation at a depth x is given by $I = I_0 e^{-\lambda x}$. If a fraction $s\,dx$ is scattered in passing through a thickness of matter dx, and k is the fraction of scattered radiation proceeding in such a direction as to enter the measuring electroscope, then if this direction is approximately normal to the surface the total intensity entering the electroscope is

$$\int_0^\infty k s I_0 e^{-2\lambda x} dx = \frac{k s I_0}{2\lambda}.$$

The same expression holds if the primary and scattered beams make equal angles with the surface of scattering substance, as was the case in these experiments. I_0 and k were the same for different radiators, λ for the emerging scattered X-radiation was determined from absorption experiments, consequently relative values of s, the scattering

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* Barkla & Ayres, Phil. Mag. Feb. 1911 ; Crowther, Camb. Phil. Soc. Proc. 1911, and Roy. Soc. Proc. 1911 ; E. A. Owen, Camb. Phil. Soc. Proc. 1911.

coefficient, were obtained from the various scattering substances. Owing to the different qualities of the fluorescent (characteristic) X-radiations from these substances, the details of the methods adopted depended upon the particular substance.

Copper.—The characteristic radiation (series K) has a wave-length about 1.5×10^{-8} cm. This was excited by all the primary radiations used, these being of shorter wave-length, consequently the complex secondary radiation was passed through a sufficient thickness of aluminium to absorb all the characteristic radiation and leave only the scattered radiation to traverse the measuring electroscope. The intensity of this, as shown by the ionization produced in the electroscope, was compared with that from aluminium when this also had been transmitted through an equal thickness of aluminium. It was seen that the two radiations measured—one from copper and the other from aluminium—after transmission through the particular thickness of aluminium were of the same penetrating power. When the radiation was soft, however, *perfect* similarity of the two secondary radiations was never obtained, though it was known that all the "K" characteristic radiation from copper was cut off. The difference in penetrating powers was, however, very small and was accounted for, as seen later, by the fact that the primary beam was not quite homogeneous, and the softer constituents were scattered from copper in somewhat greater intensity than the harder. When the primary radiation was of a penetrating type, the two secondary radiations were as nearly as measurable identical. This indicated that they were not characteristic radiations but purely scattered radiations. The thickness of aluminium used varied from about ·08 cm. to 2·2 cm. according to the penetrating power of the X-radiation experimented upon.

A series of comparisons was made between the intensities of scattered radiations, through a long series of penetrating powers of the primary radiation, by both methods mentioned above.

Silver.—The radiation of series K characteristic of silver has a wave-length about $·56 \times 10^{-8}$ cm. When a very soft primary radiation was used—one not containing an appreciable constituent of shorter wave-length—this characteristic radiation was not excited, consequently the secondary radiation from silver, after transmission through a very thin absorbing sheet in order to absorb the "L" radiation, was entirely scattered radiation. When the primary radiation became a little harder (with constituents of shorter wave-

length) the " K " radiation appeared. At this stage this had a penetrating power differing little from that of the primary and thus from that of the scattered radiation, so it became impossible to separate them by the absorption method. Consequently no values were obtained of the scattering from silver of radiation of wave-length near to that of the characteristic radiation.

When, however, radiation of very much shorter wave-length was used, the fluorescent radiation of series K was still excited, but this was removed by transmission through a sheet of aluminium, leaving only the very penetrating scattered radiation to be compared with that from aluminium. As an example of the results showing the similarity of the two penetrating radiations scattered from silver and from aluminium, the ratios of the ionizations produced by these in the two electroscopes, after transmission through various thicknesses of aluminium, are given below.

Thickness in Al traversed.	Ratio of Ionizations produced by the scattered radiations from Ag and Al in arbitrary units.
2·2 cm.	·223
1·6 ,,	·222
2·8 ,,	·219
1·6 ,,	·219

The constancy of the numbers in column 2 shows that the two radiations were transmitted through aluminium to exactly the same extent.

Tin and Lead.—The methods applied to copper and silver were used in examining the scattering from lead and tin respectively, the Cu " K " radiation being not unlike the Pb " L " radiation, and Ag and Sn " K " radiations being of neighbouring wave-length.

Considering the lack of perfect homogeneity of the beams employed, the agreement between the results obtained by the two methods was quite close. All the general features which are indicated below were shown by both methods; consequently it was unnecessary to take anything like a complete series of observations by both these methods. The second method (*b*) was subsequently adopted, so that the results given in Table II. are strictly comparable, and any irregularities occurring are not such as might be expected

to appear in the results obtained by two different methods, each giving only approximate values. The difference between the results of the two methods was usually less than 10 per cent., although in experiments from copper a variation as large as 40 per cent. was obtained. Subsequent examination of the observations taken suggests that the discrepancy was possibly due to the fluorescent radiation from the copper not having been completely absorbed in the experiments the results of which are shown by an asterisk. However that may be, the conclusions stated below hold equally well, consequently the experiments were not repeated.

Absorbability of X-radiation. $\left(\dfrac{\lambda}{\rho}\right)_{Al}.$	Relative Scattering.					
	$\dfrac{(S/\rho)_{Cu}}{(S/\rho)_{Al}}.$		$\dfrac{(S/\rho)_{Sn}}{(S/\rho)_{Al}}.$		$\dfrac{(S/\rho)_{Pb}}{(S/\rho)_{Cu}}$	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
·33					1·72	1·79
·345	*1·44	1·06				
·35			1·6	1·47		
·4					2·1	2·3
·56	*1·79	1·25^c				
·75	*1·85	1·35^c				
1·41	*2·44	2·0				
2·18	2·35	2·2				

The only results obtained by the first method (*a*) are given above along with the corresponding results by method (*b*), to show the order of agreement.

The final results of the measurements are given in Table II. The numbers given in columns 3, 4, 5 and 6 indicate the intensity of radiation scattered from copper, silver, tin, and lead relative to that scattered from aluminium; the wavelength and absorbability of the radiation are given approximately in columns 1 and 2. The absorbability of each radiation was measured by finding the thickness of aluminium necessary to diminish the ionization in the measuring electroscope by about half and applying the equation for homogeneous radiation $I = I_0 e^{-\lambda x}$. This of course gives only an approximate measure of the absorbability of a radiation not strictly homogeneous. The approximate wave-lengths were then obtained by plotting Barkla's absorbabilities against

Moseley's wave-lengths for the more homogeneous character-
istic X-radiations, and finding the wave-lengths corresponding
to the determined values of λ/ρ *.

As the scattering intensities given in Table II. are relative
to the scattering from aluminium, it remained to determine
if the amount of radiation scattered from aluminium varied
with the wave-length of the radiation. A similar deter-
mination had been made by one of us when paper and air
were the scattering substances ; in these cases little or no
variation with wave-length had been observed. It was

TABLE II.

Showing relative intensities of scattered X-radiation of
various wave-lengths from several metals.

X-radiation.		Scattering from Cu, Ag, Sn, and Pb compared with that from equal masses of Al.			
Approximate wave-length.	Approximate Absorbability $(\lambda/\rho)_{Al}$.	$\dfrac{(S/\rho)_{Cu.}}{(S/\rho)_{Al}}$	$\dfrac{(S/\rho)_{Ag.}}{(S/\rho)_{Al}}$	$\dfrac{(S/\rho)_{Sn.}}{(S/\rho)_{Al}}$	$\dfrac{(S/\rho)_{Pb.}}{(S/\rho)_{A1}}$
$\cdot96 \times 10^{-8}$ cm.	13	...	...	5·6	...
·91	11	...	3·66	...	...
·63	3·3	2·5	...	...	11·2
·59	2·8	...	...	...	11·5
·585	2·7	2·3	...	...	...
·52	1·8	2·1	...	...	9·0
·47	1·3	1·9	...	...	5·8
·43	·95	1·5	...	...	4·4
·38	·65	1·05?	...	...	2·85
·316	·37	1·12	...	...	2·65
·314	·36	1·07	1·37	...	2·1
·311	·35	...	...	1·47	...
·306	·33	...	1·25	...	1·9
·305	·32	1·05	...	...	1·7

thought possible that aluminium, an element of higher
atomic weight, might show an appreciable variation in
scattering through a long range of wave-length. The relative
intensities of the primary and scattered beams were therefore
compared by means of the ionization they produced in two
electroscopes as the wave-length of the primary radiation
was varied. The penetrating powers of both primary and
scattered radiation were also examined throughout.

* The wave-length of the most prominent line, the a line, was taken
as representing the wave-length of the K radiation sufficiently
accurately. The short wave-lengths were obtained by extrapolation.

It is not necessary to give the detailed results obtained in this investigation as some points need further examination. We have, however, established the approximate constancy of the scattering coefficient in aluminium for radiation within the range of wave-length used in these experiments.

Not only these experiments but a number of independent investigations indicate a slight increase of scattering from aluminium with an increase in the wave-length of the radiation. Within the range of wave-length of these experiments it is, however, certainly small; the error will be of no moment if we neglect it.

Conclusions.

The conclusions to be drawn from the results of Table II. may be summarized as follows :—

The scattering of X-rays of very short wave-length by equal masses of various substances varies only little with the atomic weight of the scattering element. There is a slight increase of the mass scattering coefficient with an increase in the atomic weight of the scatterer. (Elements of low atomic weight have previously been shown to scatter to approximately the same extent mass for mass not only X-radiation of short wave-length, but X-radiation of any wave-length between widely separated limits.)

The increase of the scattering with the atomic weight of the scattering substance becomes more marked with X-radiation of greater wave-length, until for long waves it becomes very considerable; that is, the heavier elements scatter much more mass for mass than light elements, when the radiation is of long wave-length ("soft").

Thus the intensity of X-radiation of given wave-length scattered by equal masses of different elements increases with the atomic weight of the element, and the intensity of X-radiation scattered from a given material increases with the wave-length of the radiation of given intensity.

As previously stated, these variations are inappreciable among elements of low atomic weight for radiations of the wave-length which may be regarded as ordinary Röntgen radiation.

In attempting to interpret these results, it should be pointed out that the scattering is proportional to the number of scattering electrons only when these act independently of one another. The condition is apparently satisfied in light atoms when traversed by Röntgen radiation of any wave-length within wide limits. Each electron is then influenced

by the electric field in the primary wave for only a very short interval of time; its actual displacement is small and the forces called into play within the atom are small; it emits energy at a rate proportional to that at which primary radiation energy passes over it*. Even in the heavier atoms in which the electrons are more closely packed, and in which they are held by stronger restraining forces as shown by their higher natural frequency of vibration, it appears that this independence in scattering action is maintained provided the primary waves are sufficiently short. Only under such conditions is the scattering coefficient in a given substance independent of the wave-length, and only then does the intensity of the scattered radiation give a direct indication of the relative numbers of electrons in the atom. It appears from the scattering of very short waves that there is little deviation even among the heavier elements from the law of approximate proportionality of the number of electrons per atom and the atomic weight. There is indication that with waves still shorter than those employed, the mass scattering coefficients would have become practically constant for all elements, showing the number of electrons per atom in the heavier elements to be of the order of half the atomic weight,—as in the case of the lighter elements.

The independent action of the electrons might be expected to disappear as the wave-length of the radiation increased. Interference with this independent scattering action might be expected to take place in the heavier atoms for shorter waves than in the case of the lighter atoms. In such a case the scattering would approximate to a scattering by groups of electrons rather than by the individual electrons. If we considered the extreme case in which n electrons might be considered as a scattering particle of charge ne, we should expect scattered radiation n times as intense as that from n independently scattering electrons †, the rate of radiation from a charged particle e being given by $\dfrac{2}{3}\dfrac{\mu e^2 f^2}{V}$, and the acceleration f being identical in the two cases. Though the actual phenomenon may only approximate to this it seems probable that the variation in size (including charge and mass) of what may be called the scattering unit is sufficient to account qualitatively for the above experimental results.

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* This, of course, does not apply to the few electrons actually ejected from atoms.

† Assuming of course the joint mass of the particle to be n times the mass of a single electron, a condition almost certainly holding with the distribution of electrons in the atom.

The magnitude of the variation, too, is as nearly as one can estimate of the right order ; and it is worth noticing that the rapid change in intensity of scattering with wave-length takes place over a range of wave-lengths approaching the diameter of the atom.

The possibility of a degradation of type—that is, a lengthening of the wave-length—of radiation in the process of scattering of long waves, and of an influence of a change of intensity of the incident radiation on the process of scattering, are points for further investigation.

We wish to express our thanks to Mr. J. E. H. Hagger— now Inspector of Munitions—for valuable help in these experiments.

XXXI. *Magnetic Rotary Dispersion in Relation to the Electron Theory. Part I. The Determination of Dispersional Periods. By* S. S. RICHARDSON, *B.Sc., A.R.C.Sc., Lecturer in Physics, Central Technical School, Liverpool* [*].

RECENT developments of the electromagnetic theory of dispersion, particularly at the hands of P. Drude, H. A. Lorentz, and M. Planck, whilst differing with respect to the mechanism to which the absorption is attributed, lead to equations which are essentially of the same form, but with constants of different meaning. The natural dispersion in regions of the spectrum not bordering on absorption bands is in each case represented by an equation of the Ketteler-Helmholtz type,—

$$n^2-1=\frac{a_1\lambda^2}{\lambda^2-\lambda_1{}^2}+\frac{a_2\lambda^2}{\lambda^2-\lambda_2{}^2}+\ \cdots\ ,\quad \cdot\ \cdot\ (1)$$

or, separating the constant from those of a purely dispersional character—

$$n^2-1=b_0+\frac{b_1}{\lambda^2-\lambda_1{}^2}+\frac{b_2}{\lambda^2-\lambda_2{}^2}+\ \cdots\quad \cdot\ \cdot\ (2)$$

In the visible and ultraviolet the effect of infra-red resonators is almost negligible and the dispersion is found to be controlled from bands lying in the ultraviolet usually, and mostly in the Schumann region. As this portion of the spectrum lies beyond the range of ordinary spectrographs, and as moreover the work of Lyman [†] has brought to light the prevalence of general absorption in this region, which

would thus add to the difficulty of detecting selective effects, in such cases the values of λ_1, λ_2, &c., can only be obtained from the dispersion curve itself. In cases where the dispersional bands lie in the near ultraviolet ($\cdot 4\,\mu$ to $\cdot 2\,\mu$), and are therefore amenable to direct experimental investigation, it is still desirable to determine the dispersional frequencies from the dispersion curve itself. For according to the theory of Lorentz-Planck the periods λ_1, λ_2, ... do not coincide with the free periods of the resonators responsible for the absorption but are sensibly shorter than the latter ; and the constants a_1, a_2, ... acquire a meaning different from that ascribed to them in the original elastic-solid and earlier electromagnetic theories. In the latter a_1, a_2, ... are proportional respectively to the number of resonators of each period in the unit volume. In the Lorentz-Planck formula we may write

$$a_1 = \frac{3g}{1-g} \quad \text{and} \quad \lambda_1{}^2 = \frac{\lambda_f{}^2}{1-g},$$

where g is proportional to the number of resonators in unit volume and λ is the wave-length corresponding to the free period. Thus

$$n^2 - 1 = \frac{\dfrac{3g}{1-g}\lambda^2}{\lambda^2 - \left(\dfrac{\lambda_f{}^2}{1-g}\right)}.$$

The well-known labours of Rubens, Nichols, Paschen, Martens and others have provided ample experimental confirmation of the application of formulæ of the type (1) or (2) above so far as natural dispersion is concerned. The observations can, however, seldom be pushed far enough into the ultraviolet to determine the differential effect of two bands in the Schumann region, and the dispersional period deduced is in most cases an effective mean value only. Denoting this by λ_1 we may write

$$n^2 - 1 = a_0 + \frac{a_1\lambda^2}{\lambda^2 - \lambda_1{}^2} - c\lambda^2, \quad . \quad . \quad . \quad . \quad (3)$$

where a_0 is the contribution made by electrons whose frequency is so high that their effect on the dispersion is too small to be detected experimentally, and $-c\lambda^2$ represents the small residual effect of infra-red resonators in the region of the spectrum to which the formula applies. As, however, there are here four adjustable constants, the formula acquires a somewhat empirical character, and it is therefore desirable

to look for confirmation of the value of λ_1 from other sources.

In a paper on "Light Absorption and Fluorescence"[*] Prof. E. C. C. Baly has shown that the dispersion of water-vapour, hydrogen chloride, chlorine, ammonia, and nitrous oxide in the visible spectrum can be accurately calculated from a simplified Sellmeier formula by taking a dispersional frequency which is some integral multiple of the frequency of some one of the infra-red bands. In the case of water-vapour for example, taking the infra-red period at $2 \cdot 95 \, \mu$, if we put $\lambda_1 = 2 \cdot 95/31$ the calculated dispersion curve is steeper than that observed; with $\lambda_1 = 2 \cdot 95/33$ it is less steep than the observation curve; but with $\lambda_1 = 2 \cdot 95/32$ the agreement is remarkably good, and it does not appear that a better result would be obtained by taking an intermediate value. Prof. Baly's argument rests upon the theory of energy quanta and the supposition that the absorbed energy is emitted at an infra-red frequency. A radiation theory of absorption appears to be quantitatively inadequate in the case of solids, but it is of course possible that some other mechanism may account for the interdependence of ultra-violet and infra-red frequencies. In Part II. of the same paper Prof. Baly points out that the central frequencies of the absorption systems in the near ultraviolet of the vapours of benzene, toluene, and the xylenes are in each case almost exact multiples of the frequencies of certain infra-red bands. If similar relations can be proved to exist in general for solids and liquids, they will provide a valuable aid in the development of optical theory. There are some indications that this may be possible. The absorption band of carbon-bisulphide at $\cdot 321 \, \mu$ corresponds to the infra-red band at $3 \cdot 2 \, \mu$ observed by Coblentz, and Martens has shown that this band ($\cdot 321$) gives rise to a small amount of selective dispersion. (*Cf.* also the result for benzene, *infra*.)

An alternative method of determining λ_1, λ_2, ... is provided by the Faraday effect, and since the application of an intense magnetic field induces a slight variation in the periods of the resonators, it is to be expected that the phenomenon of magnetic rotary dispersion may furnish information not to be obtained from natural dispersion alone.

The general effect of the application of a magnetic field to a material medium is to superpose on the existing motions of the electrons or electrified particles a uniform angular velocity $e\mathrm{H}/2m\mathrm{C}$; the effect of which, in turn, is mainly a

diamagnetic polarization. If in addition the molecules contain rotating masses of finite magnetic moment, a precessional motion will be set up in these, the extent and duration of which will depend upon the disturbing effect of collisions and therefore upon the temperature, but will be capable of developing a mean paramagnetic polarity. It may also be expected that the applied field may in many cases produce a molecular distortion, which, reacting on the vibrators, will influence their free-periods.

Sir J. Larmor's treatment of the problem of magnetic rotation * from the point of view of the first of the above effects is based on general dynamical principles and gives a result independent of the actual mechanism of dispersion. The formula obtained, namely (in symmetrical units †)

$$\delta = \frac{e}{2mC^2} \, \lambda \, \frac{dn}{d\lambda}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

is equivalent to the empirical formula of Becquerel, involves no adjustable constants, and agrees with experiment in giving rotations of the same sign on the two sides of an absorption band. It involves the assumption that the constant e/m is the same for all the resonators concerned.

If we take formula (2) for the dispersion we obtain

$$-n \frac{dn}{d\lambda} = \frac{b_1 \lambda}{(\lambda^2 - \lambda_1^2)^2} + \frac{b_2 \lambda}{(\lambda^2 - \lambda_2^2)^2} + \cdots$$

Hence

$$\delta = -\frac{e}{2mC^2} \cdot \frac{1}{n\lambda^2} \left\{ b_1 \left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2} \right)^2 + b_2 \left(\frac{\lambda^2}{\lambda^2 - \lambda_2^2} \right)^2 + \cdots \right\},$$

a summational formula of the same type as that obtained by Drude. If we assume that the summation holds good in this form with different values of e/m, we may write

$$\delta = \frac{1}{-2C^2 n\lambda^2} \left\{ \frac{b_1 e_1}{m_1} \left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2} \right)^2 + \frac{b_2 e_2}{m_2} \left(\frac{\lambda^2}{\lambda^2 - \lambda_2^2} \right)^2 + \cdots \right\} \quad (5)$$

If the infra-red bands are attributed to vibrators of atomic mass, the value of e/m for these is so small that the corresponding term vanishes from the summation, and this very completely in the visible and ultraviolet where the λ factor is very small also. If, however, any such band is due to a comparatively small number of electrons, the term must be retained. Also referring to equation (3) we see that $ndn/d\lambda$

* 'Æther and Matter,' App. F, p. 352.
† See note *infra*.

will not contain a_0, and therefore the electrons of extra-high frequency have no influence on magnetic rotation.

The effect of molecular distortion on the periods of the vibrating particles may be represented by a small change in the impressed field, as it must be proportional to the field in order that the direct proportion between δ and H observed experimentally may be retained. Representing the effective field by $(1 + \zeta)$ H, we have

$$\delta = \frac{1}{2\mathrm{C}^2 n \lambda^2} \left\{ \frac{b_1 e_1}{m_1} \left(1 + \zeta_1\right) \left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2}\right)^2 + \frac{b_2 e_2}{m_1} \left(1 + \zeta_2\right) \left(\frac{\lambda^2}{\lambda^2 - \lambda_2^2}\right)^2 + \ldots \right\} \quad (6)$$

We may note in passing that the effect denoted by ζ is similar to the effect of solvents or reagents in opening up the electromagnetic force-fields of a molecule, which has been shown by Prof. Baly to account for the development of new bands in the absorption spectrum.

Reference must here be made to Drude's earlier or molecular-current theory of magnetic rotation [*]. The phenomenon is there attributed to the displacement of the molecular orbits (or orbits of revolving electrons) about positions of equilibrium by the passing of the light-wave, such displacement being always in the wave-front. If, for simplicity, we confine ourselves to the case where the magnetic field is directed along Oz, and to plane waves propagated in this direction, an examination of Drude's analysis shows that the term responsible for the magnetic rotation arises from the periodic variation of the mean molecular field through the element of area $dy\,dz$. This variation, as Drude states, must be due to a rotation of the mean molecular field about the axis Oy, and this rotation is then represented by

$$dy\,dz \frac{d}{dz}\left(\gamma_1 \frac{d\xi}{dt}\right),$$

where γ_1 is the density of the *molecular* field and (ξ, η, ζ) the displacement of the orbit. Such a term, however, represents merely a shearing of the molecular orbits parallel to the plane xz, and would not produce a variation in the flux through the element $dy\,dz$ unless accompanied by rotation of the orbits themselves about axes parallel to Oy. Such rotation is, however, not assumed by Drude, for as he points out the magnetic field in the light-wave is too small in comparison with the field impressed in actual experimental measurements. Hence we may conclude that no effect arises in ordinary cases from orbital displacements. Moreover, as is well known, the theory requires opposite rotations on the two sides of an absorption band, and the only known

[*] ' Theory of Optics'; or *Optik*, 2te Aufl. S. 417.

instances of this are exhibited by certain absorption bands of one or two rare earths examined by G. J. Elias [*], and in those of crystals (tysonite, xenotime) at the temperature of liquid air brought to light by the remarkable experiments of J. Becquerel [†]. These isolated instances (the substances are all paramagnetic) doubtless arise from some other cause. Becquerel, in fact, explains them as due to positively charged vibrators combined with differential absorption.

In the case of very strongly magnetic substances cohesion between the components of a molecular chain might induce an appreciable variation of flux through orbital displacements, and it is possible that the rotation observed by Kundt in transparent films of iron and other magnetic metals may be due to this cause. In view of the fact that the wave-length of light is some 10^3 molecular diameters, no effect is to be expected from such cohesion, except in the case of ferro-magnetic metals. In general, therefore, the orbital displacement will be without effect.

A modification of equation (4) has been introduced by Ulfilas Meyer [‡], namely,

$$\delta = -\frac{e}{2mC^2}\frac{n'}{n}\lambda\frac{dn'}{d\lambda}.$$

In this expression n' is such that $n'^2 - 1$ is the value of the right-hand member of (1) when the terms corresponding to the infra-red periods are omitted. It is deduced from the Hall-effect formula of Drude by omitting the infra-red and high-frequency terms and assuming that e/m has the same value for all the terms retained. Meyer obtains a good agreement between theory and experiment in the case of sylvin, rock-salt, and fluor-spar.

In what follows we shall retain the summational formula. Putting

$$z_1 = \left(1 + \zeta_1\right)\frac{e_1}{m_1}, \qquad z_2 = \left(1 + \zeta_2'\right)\frac{e_2}{m_2},$$

we have

$$\delta = \frac{1}{2n\lambda^2C^2}\left\{b_1z_1\left(\frac{\lambda^2}{\lambda^2-\lambda_1^2}\right)^2 + b_2z_2\left(\frac{\lambda^2}{\lambda^2-\lambda_2^2}\right)^2 + \ldots\right\}, \quad (7)$$

or setting $\phi = n\delta\lambda^2$ and $k_1 = \dfrac{b_1z_1}{2C^2}$, &c.,

$$\phi = k_1\left(\frac{\lambda^2}{\lambda^2-\lambda_2^2}\right)^2 + k_2\left(\frac{\lambda^2}{\lambda^2-\lambda_2^2}\right)^2 + \ldots \quad \cdot \quad \cdot \quad (8)$$

[*] *Ann. d. Phys.* (35) p. 299 (1911).
[†] *Phil. Mag.* xvi. p. 153 (1908).
[‡] *Ann. d. Phys.* (30), p. 607 (1909).

For substances which are transparent in the visible and near infra-red, and for which the infra-red values of z are negligible, $\lambda_1, \lambda_2 \ldots$ will represent ultraviolet periods only. If λ_2 is considerably less than λ_1, then since $b_1 = a_1\lambda_1^2$, $b_2 = a_2\lambda_2^2$, the ratio b_2/b_1 and therefore k_2/k_1 will be much smaller than a_2/a_1. Further, the ratio

$$\frac{\lambda^2}{\lambda^2 - \lambda_1^2} \quad : \quad \frac{\lambda^2}{\lambda^2 - \lambda_2^2}$$

(if $\lambda > \lambda_1$) will be less than its square. *The effects of two free-periods are therefore more sharply differentiated in magnetic rotary dispersion than in ordinary dispersion.* Further, the resonators which give rise to the constant term a_0 in (3) have no appreciable effect on magnetic rotation, and these therefore do not give rise to the term k/λ^2 in the expression for δ as is sometimes stated [*]. Hence the values of $\lambda_1, \lambda_2 \ldots$ in (8) are those of the *dispersional* periods only in the ultraviolet. If there is only one such period we have

$$\phi = k\left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2}\right)^2. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

If now this equation is used to determine λ_1 from a series of values of λ, say approximately equally spaced along the spectrum, the values so obtained should agree within the limits of experimental error with the value of λ_1 obtained from natural dispersion if there is only one free-period. Want of such agreement, particularly if accompanied by a progression in the calculated values of λ_1, indicates the existence of at least two free-periods. In the latter case, and where sufficient progression exists, a closer approximation to λ_1 may be obtained by neglecting the dispersional part of

$$k_2\left(\frac{\lambda^2}{\lambda^2 - \lambda_2^2}\right)^2$$

whilst retaining its constant part. Equation (8) may then be written

$$\phi = k_1\left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2}\right)^2 + k_2 \quad \cdot \quad \cdot \quad \cdot \quad (10)$$
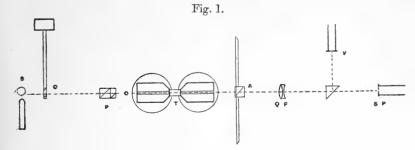
and λ_1, k_1, k_2 deduced from three values of ϕ.

In the experiments recorded below I have carried the measurements of magnetic rotation as far into the ultraviolet as the nature of the liquids used and the apparatus at my disposal would allow, as it seemed probable that an extended dispersion curve would give in most cases more information concerning the dispersional-periods than one confined to the visible spectrum.

* *Cf.* Wood's 'Physical Optics,' p. 530.

Experimental.

The method adopted is the same in general principle as that already used by several experimenters *, and consists of the use of a half-shade polarimeter in conjunction with a spectroscope, which may be placed so as to disperse the light either before or after the transmission through the polarizing prisms. In the former case the spectroscope takes the form of a monochromatic illuminator. As the theory of the half-shade method has been discussed elsewhere †, remarks here may be confined to a description of the disposition of the apparatus which has been found most suitable for measurements in the visible and ultraviolet.

The light from the source S (fig. 1) passes first through a quartz-condensing lens of 20 cm. focal-length, and is concentrated by this on the aperture O in the electromagnet, the ultraviolet rays coming to foci between this aperture and the polarizing prisms P. After traversing the substance in T and the analyser A, the rays are collected by a quartz-fluorite lens QF which forms a sharp image of the dividing-line of the polarizer on the slit V of a wave-length spectrometer of the constant-deviation type. The rays are deflected to this slit by a totally-reflecting glass prism which is mounted so that it can be racked down out of the path of

Fig. 1.

the light when required. In this case the light falls directly on the slit of a quartz-spectrograph SP. With this arrangement the condition of the illumination could be tested at any time during a series of photographic exposures, a great convenience when using sources of variable intensity. As the prism of the constant-deviation spectrometer absorbs somewhat strongly in the violet, the visual observations were not continued beyond $\lambda = \cdot 4958\,\mu$. Observations on

* Landau, *Phys. Zeits.* p. 417, 1908; and Lowry, Proc. Roy. Soc. 1908, A, p. 472.
† Landau, *loc. cit.*, and G. J. Elias, *Ann. der Phys.* (35) p. 299 (1911).

this wave-length were made both visually and photo-graphically.

The magnet available gave only a comparatively small potential (5000 cm.-gauss with a 1 cm. gap), the polar faces being 3 cm. square. Reduction of this by additional cones was found not to increase the magnetic potential ; the set-back of the main pole-pieces which their introduction entailed counteracted the effect of concentration of the field. The pole-pieces were bored with holes which, in order to preserve the uniformity of the field, were only ·25 inch in diameter. Preliminary experiments both with an ex-ploring coil and by magnetic rotation showed that the magnetic potential increased with increasing interpolar distance up to 4 cm. gap and then diminished. The tube used for most of the liquids tested had a length 3·62 cm. A current of 7·5 amperes was used which carried the magnetization a little beyond the " knee " of the curve. No advantage can be gained by the use of stronger currents, since the small increase of field is obtained at the expense of a rapid increase in the heating of the magnet coils. With the above current the coils were only just warm to the touch after a 2 hours' run. The current was obtained from a battery of 50 accumulators, and as the resistance of the magnet coils and battery leads was only 1·63 ohm, by the use of a large ballasting resistance the current could be maintained constant to 1 part in 750 for several hours at a time. The ballast consisted of four open coils of bare eureka 16 S.W.G., each 2 metres long and about 5 cm. diameter. These were arranged in series with two parallel wires of the same material and gauge, which, with a spring brass connector, formed an exceedingly convenient and reliable fine adjustment. The current was measured with a millivolt-amperemeter by Siemens.

A change in the field-strength may be produced through the heating of the magnet cores. A careful ballistic test showed, however, that with a current of 7·5 amperes the error due to this cause would be quite negligible.
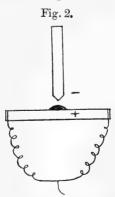
The polarizing prisms were of the square-ended Foucault type permitting complete polarization of a beam of small angular diameter to about λ ·220 μ, and were supplied by Hilger. A two-part polarizer was employed, the angle of half-shade being adjustable. For most of the spectrum lines selected an angle of 1°·5 could be used, but owing to the narrow aperture in the pole-pieces and the consequent reduction of the intensity of the light, it was not found to be advisable to reduce the angle below this value.

The condensing lens C was mounted upon an electrically-driven tuning-fork of frequency 30. The lens was thus maintained in vibration in a vertical plane, and the light distributed more uniformly over the field of the polarizer. The use of a lens vibrating harmonically, though possibly open to theoretical objections, was in actual practice found to render the results much more consistent and reliable.

The projection lens was a quartz-fluorite combination of 32 cm. focal-length, giving exceedingly good achromatism through the ultraviolet spectrum. It was corrected for spherical aberration at $\cdot300\,\mu$.

A suitable source of light of the required intensity for this type of experiment is difficult to find. A quartz-mercury lamp possesses many advantages, but lines of the requisite intensity are not very evenly spaced along the spectrum. Probably the best source is a quartz-tube amalgam lamp, but in the absence of the latter and after trials with a simple mercury lamp, it was decided to use the iron arc as the source. The difficulty here is to obtain sufficient steadiness. Owing to the relatively large current which must be used, the negative pole melts, a circumstance which, it was found, prevents the use of a rotating arc, excellent as this is for ordinary spectrographic work. Iron-magnetite, and iron-cassiterite arcs were also tried, but it was ultimately found that the best work could be done with a simple iron arc arranged as in fig. 2. The negative electrode is vertical and

Fig. 2.

adjustable while the positive is horizontal and connected to the circuit at both ends through equal manganin resistances, R_1, R_2. A current of 7 to 8 amperes was used with poles $1\cdot5$ cm. in diameter. With this arrangement, once the poles become thoroughly hot, the molten iron from the negative

falls and forms a very symmetrical button on the positive and the arc remains in consequence very steady over long periods.

The tube to contain the liquids under test was about 1·5 cm. diameter, the ends being ground square and smooth. To avoid contamination no cement was used, the end plates being held on by placing between the tube-ends and the poles two small rubber rings of the same diameter as the tube. For the ultraviolet, plates of fused silica were at first employed, but were found after a time to develop strains introducing a small amount of elliptic polarization which would reduce the sensitiveness of the apparatus. For the experiments recorded below microscope cover-glasses ·01 cm. thick have been employed. These transmit quite well to ·275 μ.

The temperature was observed with a copper-constantan thermocouple in series with a suspended-coil galvanometer, preliminary experiments showing that the E.M.F. of this couple was not affected by the magnetic field employed. The cold junction was kept in ice. The tube containing the liquid was enclosed in a cubical box at the bottom of which was a small heater consisting of 50 cm. of No. 24 constantan wound on a rectangular frame. This coil was joined in series with an accumulator, amperemeter, and sliding rheostat. It was thus found possible to maintain the tube at a temperature of 20° C. within a few tenths of a degree. As the heating effect in the magnet coils was scarcely perceptible, the above method of maintaining the liquid at a constant temperature was as a rule practicable for a 2 hours' run. The small temperature variations allowed could be neglected on account of the small effect of temperature on magnetic rotation.

The scale attached to the analyser mounting could be read to 1′, but most of the readings were taken on an accessory " quartz-scale " (100 divisions = 21° 40′) with vernier reading to 1′·3. The disposition of the apparatus shown in fig. 1 allows the settings to be made by the observer at the spectrometer. In the visual region the value of the rotation for each line was deduced by taking the mean from 72 settings of the analyser, the current being reversed after each group of 6 settings. The extreme variation in the readings was seldom more than 4′ and with the brighter lines much less than this. The values of δ quoted in the tables below are probably correct to the third significant figure where the magnet was used, and to 1 part in 1000 with the solenoid.

In the ultraviolet, when using a spectrum rich in lines, a choice of two methods may be made. (1) A particular line may be selected and a photograph taken for each one of a number of settings of the analyser. Provided the latter are not too far apart ($3'$ or $4'$) the particular reading which gives equality of illumination in the upper and lower spectra can be ascertained with the same degree of accuracy as in visual observations. (2) The analyser may be set to a given position, and the particular line with equal density in the two spectra may then be found by inspection. The latitude of error in the former method is clearly independent of the rotary dispersion and depends only upon the light-intensity and the degree of half-shade. But in the latter method, although the accuracy is increased by reducing the angle of half-shade, it also depends to a large extent upon the luminosity-gradient along the spectrum, and therefore upon the rotary dispersion. If this is small, as it is with small magnetic potential, there is difficulty in locating the position of exact equality of illumination. For obtaining the rotation corresponding to an accurately known wave-length, therefore, the former procedure is to be preferred. When, however, the dispersion-curve is viewed as a whole, the limits between which it may vary through experimental errors are not very different in the two cases, and for the same reason no advantage accrues from a steepening of the luminosity gradient with an auxiliary plate of quartz or other optically active substance. In the present investigation, where the electro-magnet has been employed, the first method has been used to obtain the final results, the second being applied in most cases only to the preliminary or "pilot" plates. The following lines were selected as being (*a*) sufficiently monochromatic, (*b*) of considerable intensity, and (*c*) nearly equally spaced along the spectrum :—

6708 (Li), 5893 (Na), 4958 (Fe), 4529 (Fe),
4046 (Fe), 3631 (Fe), 3306 (Fe), 3100 (Fe).

Wratten Double-Instantaneous plates were used throughout, the delicacy and fine grain of the film being well suited to this class of work. The exposures necessary varied from 15 seconds to 2 minutes.

The correction for the end-plates, being only just outside the limits of experimental error, was obtained with sufficient accuracy by calculation from the law of the inverse square ($\delta \propto \lambda^{-2}$), the mean rotation of glass for the D line being taken as $\cdot016'$.

As very satisfactory extinction was obtained with crossed nicols, it was concluded that no appreciable quantity of doubly-reflected light entered the spectroscope and no correction was deemed necessary. In introducing such corrections on theoretical grounds only there is danger of over-correction, as absorption within the substance under test during the double transit or a very slight want of parallelism between the end-plates would prevent the reflected light from entering the spectroscope-slit.

From the observations on pure carbon bisulphide for the D line, and at 20° C., using the value for Verdet's constant obtained by Rodger and Watson [*] :

$$\delta = \cdot04347 - \cdot0_4737 \, t,$$
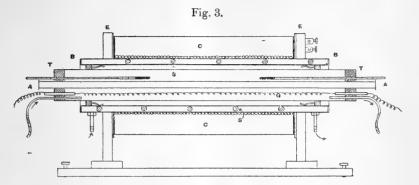
the change of magnetic potential on reversal of the field (C = 7·5 amperes) was found to be 13,322 cm.-gauss.

Experiments with a Solenoid.—For liquids which can be obtained in considerable quantities and which are sufficiently transparent in long columns, a solenoid possesses several advantages over an electromagnet. A much larger magnetic potential is easily obtained, with consequent increase in rotation and dispersion ; and if the ends of the experimental tube are allowed to project beyond the ends of the coil, the method lends itself particularly to the determination of absolute rotations [†]. For measurements of the rotary dispersion the chief disadvantage is that the field is strictly proportional to the current-strength, and it is therefore necessary to keep the latter more nearly constant than when using a magnet with iron cores brought nearly to saturation; and the large resistance of a solenoid leaves little room for ballasting resistance unless a battery of an exceptionally large number of cells is available. The heating of the coils causes a rapid decrease in the current, but I find that with a water-cooled coil the variation of current is very small after the initial stage of the heating provided the flow of water is steady, and with the aid of a small rheostat can be kept constant to within 1 part in 1000 by occasional adjustment. A diagram of the coil designed for use with a battery of 50 accumulators and for a current of 7·5 amperes is given in fig. 3. A brass tube B, 7·7 cm. in diameter, is mounted on two ebonite uprights E, 1·6 cm. thick and 21 cm. high. The tube is attached to the ebonite by means of two brass flanges, the inner faces of which are lined with fibre. The coil,

[*] Phil. Trans, A, 1895.
[†] *Ibid.*

consisting of 3750 turns of No. 18 double cotton-covered copper wire in 12 layers, is wound in the space C between the fibre cheeks, each layer being carefully insulated with shellac (which was then dried by passing a current). The ends of alternate layers are brought out to separate terminals

Fig. 3.

on the ebonite uprights. The finished coil is 11 cm. external diameter and 50 cm. long. The tube B carries an inner one of 6 cm. internal diameter, the space between the two being closed by rings at the ends, so forming a space for circulation of the cooling-water. A thin brass rod bent into a helix S is fitted between the tubes to give a spiral motion to the flow of water. The tube to contain the liquid under examination, A, is mounted in a wider tube T forming a water-jacket, the latter being held in position in the inner brass tube by means of brass collars provided with spring clips. The water-jacket carries also two thermometers, and a spiral of No. 24 constantan. By means of the latter coil, which was connected to an accumulator, amperemeter, and rheostat, it was possible to maintain the temperature constant within one or two tenths of a degree. A temperature of 20° was chosen for all the experiments. The disposition of the remainder of the apparatus was the same as in fig. 1, the coil taking the place of the magnet. By choosing a suitable position for the projecting lens OF, it was possible to keep the light reflected from the inner surface of the tube quite clear of the upper and lower extremities of the slit of the spectrometer.

The insulation of the coil was carefully tested, both between successive layers and between these and the brass tube, under a pressure of 100 volts. No leakage could be detected except in the case of the bottom layer, which was not used in the experiments.

Water.

Pure conductivity water only was used and the rotation was measured with the solenoid. For the ultraviolet the values were deduced from the photographs by the second method described above, and these were converted into absolute rotations by the use of Rodger and Watson's value for the D line. The refractive indices n given in the table are those of Gifford * corrected for the temperature difference $20°-15°$ C. The change of magnetic potential on reversal was 42,238 cm.-gauss, giving a doubled rotation of over $9°$ for $\lambda = \cdot5893$ and nearly $43°$ for the line $\cdot3034$.

For convenience of reference in this and the following tables the observations for different wave-lengths are distinguished by the letters a, b, c, etc.

Obs.	$\lambda \times 10^4$.	$\delta \times 10^6$.	n_{20}.	$\phi \times 10^{14}$ (obs.).	$\phi \times 10^{14}$ (calc.).	$\Delta\phi$.
a	$\cdot5893$ (Na)	$3\cdot808$	$1\cdot3330$	$1\cdot763$	$1\cdot764$	$+1$
b	$\cdot4958$ (Fe)	$5\cdot529$	$1\cdot3366$	$1\cdot816$	$1\cdot816$	0
c	$\cdot4678$ (Cd)	$6\cdot276$	$1\cdot3381$	$1\cdot838$	$1\cdot839$	$+1$
d	$\cdot4341$ (H)	$7\cdot431$	$1\cdot3403$	$1\cdot877$	$1\cdot875$	-2
e	$\cdot3962$ (Al)	$9\cdot159$	$1\cdot3435$	$1\cdot931$	$1\cdot929$	-2
f	$\cdot3611$ (Cd)	$11\cdot389$	$1\cdot3475$	$2\cdot002$	$2\cdot001$	-1
g	$\cdot3303$ (Zn)	$14\cdot218$	$1\cdot3523$	$2\cdot098$	$2\cdot091$	-7
h	$\cdot3034$ (Sn)	$17\cdot620$	$1\cdot3580$	$2\cdot203$	$2\cdot206$	$+3$

The values of λ_1 calculated from equation (9) are

$$ab = \cdot109$$
$$bd = \cdot111 \qquad ad = \cdot110$$
$$df = \cdot112 \qquad dh = \cdot114$$
$$fh = \cdot114.$$

The values of λ chosen for the calculation must be as widely separated as possible, as the effect of a small experimental error becomes greatly magnified when λ_1 is calculated from two points on the dispersion curve which lie too close together.

Lowry† has determined the dispersion ratio of the magnetic rotations for the two mercury lines $\cdot5461$ and $\cdot4359$ for water and a number of aliphatic compounds, using a very powerful magnet. In the case of water,

$$\frac{\delta_{(4359)}}{\delta_{(5461)}} = 1\cdot645.$$

* Proc. Roy. Soc. Ser. A, lxxviii.
† Jour. Chem. Soc., Jan. 1914.

Taking $n_{(5461)} = 1.3345$ and $n_{(4359)} = 1.3402$, formula (9) gives $\lambda_1 = .113\,\mu$, a value agreeing well with the above.

A small but decided progression is apparent in the values of λ_1, which points to the existence of at least two free-periods responsible for the dispersion in water. The smallness of the progression is probably due to the value of λ_1 being small in comparison with the shortest λ of the experiments, and for the same reason the longer free-period cannot be calculated with accuracy from equation (10). The mean value obtained from observations *acf* and *beh* is approximately $.1375\mu$, which gives $k_1 = .9499$ and $k_2 = .7012$. Thus

$$\phi \times 10^{14} = .9499 \left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2} \right)^2 + .7012, \quad \lambda_1^2 = .01891.$$

The differences between the values of ϕ calculated from this formula and the observed values are given in the last column.

Flatow [*] finds that the natural dispersion in water is very accurately represented by an equation of the form (3) from $.589$ to $.214\,\mu$; the constants for $20°$ C. being :

$$a_0 = .37512 \qquad c = .013414$$
$$a_1 = .38850 \qquad \lambda_1 = .12604.$$

As λ_1 is here an effective mean value, this result agrees well with the deduction made above, namely, that the dispersion in liquid water is controlled by a period near $\lambda = .1375$ and at least one other of smaller value.

The following table gives the values of the magnetic rotation (δ) relative to the value for $.4958\mu$ for a number of lines in the ultraviolet spectrum of iron. The only previously obtained values—those of Landau [†]—obtained with an electromagnet of small power, and recorded to three significant figures, are worked out as ratios for comparison.

$\lambda \times 10^4$.	δ (Landau).	δ (Author).
.4958	1.000	1.000
.4529	1.226	1.221
.4405	1.301	1.299
.4308	1.366	1.365
.4199	1.446	1.449
.4046	1.575	1.576
.3886	1.737	1.733
.3609	2.065	2.060
.3100	3.005	3.017

* *Ann. d. Phys.* (12) p. 85 (1903).
† *Phys. Zeits.* (13) p. 417 (1908).

Benzene.

In the case of benzene and the liquids following, the electromagnet was employed in order to reduce absorption by the use of a short column of liquid. The values of n are deduced from the observations of Simon. The values of δ are here all obtained from the photographs, the analyser settings being varied from each line until equality of illumination was obtained. $t = 20^\circ$ C. The absolute rotations are obtained by using Perkin's water-ratio for the D line (2·3053).

Obs.	$\lambda \times 10^4$.	$\delta \times 10^6$.	n_{20°	$\phi \times 10^{14}$.
Ref. ...	·5893	8·778	1·5004	4·574
a	·4529	16·49	1·5187	5·137
b	·4046	22·21	1·5311	5·567
c	·3631	30·32	1·5475	6·186
d	·3306	40·95	1·5670	7·014
e	·3100	51·51	1·5850	7·846

Calculating the values of λ_1 from equation (9) we find progressive values, namely :—

$$ab = ·1662 \qquad ac = ·1681$$
$$bc = ·1694 \qquad bd = ·1716$$
$$cd = ·1734 \qquad ce = ·1747$$
$$de = ·1762.$$

As the amount of increase is here considerable, at least two free-periods probably widely separated may be expected. Using equation (10) to obtain a closer approximation to the longer period, we obtain :—

$$\left. \begin{aligned} \text{from } bce, \quad \lambda_1 &= ·1907 \\ ace, \quad \lambda_1 &= ·1903 \\ bde, \quad \lambda_1 &= ·1897 \end{aligned} \right\} \text{Mean} = ·1902\mu. \quad \lambda_1^2 = ·03618.$$

$$k_1 = 2·468, \qquad k_2 = 1·498.$$

Thus $\qquad 10^{14}\phi = 2·468 \left(\dfrac{\lambda^2}{\lambda^2 - ·03618} \right)^2 + 1·498.$

The differences between the values of ϕ calculated from this and the observed values are given below.

$\lambda \times 10^4$.	ϕ (obs.).	ϕ (calc.).	Diff.
·5893	4·574	4·574	(ref.)
·4529	5·137	5·137	0
·4046	5·567	5·566	−1
·3631	6·186	6·187	+1
·3306	7·014	7·013	−1
·3100	7·846	7·847	+1

The natural dispersion in benzene has been measured by Simon * in the visible and ultraviolet, and by Rubens in the infra-red. I find the results well represented by formula (3), taking the mean effective dispersional period at ·1815 μ, and $a_1 = ·62871$, $a_0 = ·55695$, $c = ·0017$. Thus :

$$n^2 - 1 = ·55695 + \frac{·62871\,\lambda^2}{\lambda^2 - \lambda_1^2} - ·0017\,\lambda^2.$$

The differences between the observed and calculated values are given in the table below.

Obs.	$\lambda \times 10^4$.	n (obs.).	n (calc.).	Diff. (Author).	Diff. (Martens).
SIMON.	·2837	1·6190	1·6190	0	0
	·2881	1·6120	1·6122	+2	+5
	·2981	1·5983	1·5986	+3	+10
	·3404	1·5603	1·5605	+2	+12
	·3467	1·5564	1·5565	+1	+11
	·3613	1·5485	1·5484	−1	+8
	·4341	1·5229	1·5227	−2	0
	·4678	1·5158	1·5155	−3	−3
	·4800	1·5137	1·5136	−1	−5
	·4861	1·5125	1·5123	−2	−3
	·5086	1·5094	1·5090	−4	−7
	·5349	1·5060	1·5056	−4	−8
	·5893	1·5005	1·5003	−2	−8
	·6563	1·4959	1·4957	−2	−11
	·7682	1·4907	1·4905	−2	−12
RUBENS.	·810	1·4890	1·4892	+2	−8
	·864	1·4874	1·4873	−1	−8
	·926	1·4859	1·4864	+5	−7
	·997	1·4848	1·4851	+3	−8
	1·080	1·4834	1·4839	+5	−6
	1·178	1·4822	1·4826	+4	−5
	1·297	1·4813	1·4817	+4	−6
	1·439	1·4801	1·4806	+5	−2
	1·621	1·4792	1·4796	+4	−1
	1·850	1·4784	1·4785	+1	0

It will be seen that since the mean dispersional period ·1815 μ is considerably greater than the mean of the values obtained above from formula (9), Meyer's equation cannot apply strictly in the case of benzene. A similar remark applies to the liquids water, metaxylene, naphthalene bromide, and carbon bisulphide.

Martens [*] deduces a formula for benzene in which $a_0 = \cdot4528$, $a_1 = \cdot7264$, $c = 0$, and $\lambda_1 = \cdot1745$. The differences for this formula are given in the last column above.

Prof. Baly associates the central line of the absorption spectrum of benzene vapour (·2466) with the infra-red band observed by Coblentz at 2·49 μ, the ratio being nearly 1 : 10. In this connexion it is worth notice that the principal dispersional period deduced above from the magnetic rotation ·1902 μ, is almost an exact submultiple of 2·49 μ, the ratio being 1 : 13.

The absorption bands of benzene in the near ultraviolet with a centre at ·2466 μ have very little effect on the dispersion or magnetic rotation. Introducing a term for this band, I find that the constant k is only 1/740 of the sum of the remaining constants. The absorption is here clearly due to a comparatively small number of electrons. A probable explanation being that the period ·2466 is only acquired by one or more electrons in the molecule at comparatively rare intervals, due to an accidental distortion of the molecule through collision. M. Henri [†], from photometrical measurements, finds that in acetone only one molecule in 36 is effective in producing the characteristic bands of this substance, and Baly and Tryhorn have recently obtained a similar result for aniline.

m. *Xylene.*

The observations were conducted in the same manner as

Obs.	$\lambda \times 10^4$.	$\delta \times 10^6$.	n_{20°.	$\phi \times 10^{14}$.
a	·6708	5·416	1·4914	3·634
b	·5893	7·210	1·4965	3·747
c	·4958	10·84	1·5061	4·014
d	·4529	13·51	1·5131	4·194
e	·4046	18·19	1·5242	4·538
f	·3631	24·72	1·5381	5·014

[*] *Ann. d. Phys.* (6) p. 603 (1901).
[†] *Phys. Zeits.* p. 515 (1913).

those for benzene. The values of n are deduced from Rubens' measurements. $t = 20°$ C.

The absolute values are obtained from Perkins' water-ratio for the D line (1·8957).

Using equation (9) the values of λ_1, from sufficiently separated values of λ, are progressive.

$$ac = ·1571$$
$$bd = ·1588$$
$$ce = ·1614$$
$$df = ·1653$$

$$ad = ·1534$$
$$be = ·1613$$
$$cf = ·1633$$

The existence of at least two dispersional frequencies is thus indicated. Proceeding to apply equation (10) we obtain

$$\text{from } ace, \quad \lambda_1 = ·1819$$
$$bdf, \quad \lambda_1 = ·1886.$$

The second value obtained from the larger values of δ is more probably free from the effect of experimental error. Using this value, $k_1 = 1·9916$, $k_2 = 1·2790$. Thus

$$10^{14} \times \phi = 1·9916 \left(\frac{\lambda^2}{\lambda^2 - ·03557} \right)^2 + 1·279.$$

$\lambda \times 10^4$.	ϕ (obs.).	ϕ (calc.).	Diff.
·6708	3·634	3·627	−·007
·5893	3·747	3·751	+·004
·4958	4·014	4·002	−·012
·4529	4·194	4·194	·000
·4046	4·538	4·530	−·008
·3631	5·014	5·014	·000

From Simon's * values for the natural dispersion of m. xylene in the ultraviolet I find

$$a_0 = ·61444, \quad a_1 = ·56073, \quad c = ·00054,$$

the mean effective value of λ_1 being ·1830. Thus

$$n^2 = 1·61444 + ·56073 \frac{\lambda^2}{\lambda^2 - ·03349} - ·00054 \lambda^2.$$

* *Loc. cit.*

In the following table the infra-red values are those of Rubens, whose values are reduced by ·0011 in order to bring them into line with those of Simon.

	$\lambda \times 10^4$.	n (obs.).	n (calc.).	Diff.
SIMON.	·2981	1·5861	1·5856	−5
	·3081	1·5751	1·5750	−1
	·3133	1 5701	1·5702	+1
	·3261	1·5596	1·5598	+2
	·3404	1·5501	1·5502	+1
	·3467	1·5464	1·5465	+1
	·3613	1·53905	1·53905	0
	·4340	1·5154	1·5154	0
	·4678	1·5089	1·5087	−2
	·4800	1·5069	1·5068	−1
	·4861	1·5059	1·5059	0
	·5086	1·5030	1·5028	−2
	·5349	1·4999	1·4998	−1
	·5893	1·4950	1·4949	−1
	·6563	1·4908	1·4907	−1
	·768	1·4860	1·4860	0
RUBENS (Diff. −11).	·823	1·4857	1·4846	0 (−11)
	·878	1·4845	1·4833	−1
	·940	1·4834	1·4822	−1
	1·012	1·4822	1·4811	0
	1·096	1·4808	1·4801	+4
	1·195	1·4795	1·4791	+7
	1·316	1·4784	1·4783	+10
	1·461	1·4775	1·4775	+11
	1·645	1·4768	1·4784	+27
	1·881	1·4760	1·4760	+11

From Rubens' values Martens deduces $\lambda_1 = \cdot 1366$. But this value is clearly much too small, the differences for ·3403, ·3261, ·3133, ·3081 being respectively −16, −33, −56, and −69. Martens assumes $a_0 = 0$, $c = 0$, and takes $a_1 = 1 \cdot 1724$.

The sudden bend in the experimental curve in the region of $\lambda = 1 \cdot 645$ is doubtless due to selective dispersion produced by the band observed by Coblentz at $1 \cdot 7 \mu$. Similar but smaller fluctuations appear in the experimental curve for benzene, for which substance Coblentz has recorded weak bands at $\cdot 8 \mu$, $1 \cdot 0$, $1 \cdot 4$, and $1 \cdot 7$.

Naphthalene Bromide.

The liquid used was a specimen of α-monobromnaphthalin, supplied by Kahlbaum as pure, and carefully redistilled.

The values of n are deduced from the observations of Simon [*].
$t = 20°$.

Obs.	$\lambda \times 10^4$.	$\delta \times 10^6$.	n_{20}.	$\phi \times 10^{14}$.
a	·6708	17·64	1·6475	7·858
b	·5893	23·83	1·6576	8·283
c	·4958	38·21	1·6783	9·370
d	·4529	50·19	1·6942	10·296
e	·4046	74·36	1·7231	12·17
f	·3735	105·4	1·7531	14·70

The values of λ_1 deduced from equation (9) are progressive.

$$ac = ·2054 \qquad ad = ·2087$$
$$bd = ·2120 \qquad be = ·2166$$
$$ce = ·2198 \qquad cf = ·2268$$
$$df = ·2298$$

The exceptionally high value of λ_1 combined with the high density (1·487) of the liquid accounts for the very large magnetic rotation produced.

Proceeding to estimate the value of the larger dispersional period from equation (10) we obtain :—

$$\text{from } ace, \quad \lambda_1 = ·2532,$$
$$bdf, \quad \lambda_1 = ·2563.$$

The latter value gives $k_1 = 3·1286$, $k_2 = 3·5245$; and the former gives $k_1 = 3·2151$, $k_2 = 3·4858$.

Taking the value obtained from the larger rotations as the more accurate, we have

$$\phi \times 10^{14} = 3·1286 \left(\frac{\lambda^2}{\lambda^2 - ·06569} \right)^2 + 3·5245.$$

$\lambda \times 10^4$.	ϕ (obs.).	ϕ (calc.).	Diff.
·6708	7·858	7·814	−·044
·5893	8·283	8·283	·000
·4958	9·370	9·351	−·019
·4529	10·296	10·295	−·001
·4046	12·17	12·25	+·08
·3735	14·70	14·70	·00

* *Loc. cit.*

For the natural dispersion in this liquid Walter's [*] values have been taken (to four decimal places) and appear to be fairly represented by a mean period $\lambda = \cdot2370$, the formula I obtain being:

$$n^2 - 1 = \cdot95422 + \cdot66659 \, \frac{\lambda^2}{\lambda^2 - \cdot05617}.$$

$\lambda \times 10^4$.	n (obs.).	n (calc.).	Diff.
$\cdot7621$	$1\cdot6405$	$1\cdot6408$	$+3$
$\cdot6884$	$1\cdot6464$	$1\cdot6463$	-1
$\cdot6563$	$1\cdot6495$	$1\cdot6495$	0
$\cdot5893$	$1\cdot6582$	$1\cdot6581$	-1
$\cdot5270$	$1\cdot6705$	$1\cdot6703$	-2
$\cdot4861$	$1\cdot6819$	$1\cdot6819$	0
$\cdot4341$	$1\cdot7041$	$1\cdot7041$	0
$\cdot4308$	$1\cdot7059$	$1\cdot7059$	0
$\cdot4102$	$1\cdot7185$	$1\cdot7190$	$+5$
$\cdot3970$	$1\cdot7289$	$1\cdot7291$	$+2$

Carbon Bisulphide.

The liquid used was purified by allowing it to stand in contact with mercuric chloride for several weeks, with subsequent repeated distillation over mercury. The product was almost odourless. The values of n were deduced from those of van der Willigen. In this case the observations were confined to the visible spectrum. $t = 20°$.

Obs.	$\lambda \times 10^4$.	$\delta \times 10^6$.	n_{20}.	$\phi \times 10^{14}$.
a	$\cdot6708$	$14\cdot68$	$1\cdot6182$	$6\cdot604$
b	$\cdot5893$	$19\cdot90$	$1\cdot6291$	$6\cdot912$
c	$\cdot4958$	$30\cdot71$	$1\cdot6508$	$7\cdot550$
d	$\cdot4326$	$44\cdot59$	$1\cdot6775$	$8\cdot344$
e	$\cdot4144$	$50\cdot50$	$1\cdot6885$	$8\cdot653$
f	$\cdot4046$	$54\cdot14$	$1\cdot6952$	$8\cdot863$

The first three observations were obtained by the visual method, the latter three photographically.

[*] *Ann. d. Phys.* 1891.

The values of λ_1 calculated from equation (9) are

$$ac = 1803$$
$$bd = 1816 \qquad \text{Mean } \lambda_1 = 1804.$$
$$ce = 1805$$
$$df = 1793$$

No progression is here shown, formula (9) thus representing the magnetic dispersion with sufficient accuracy within the visible spectrum. Verdet's values for the D and F lines of the solar spectrum give a value quite near to the above.

$$\delta_D/\delta_E = \cdot768, \quad n = 1\cdot6291 \left.\right\} \lambda_1 = \cdot1861.$$
$$\delta_F/\delta_E = 1\cdot234, \quad n = 1\cdot6538$$

The value so obtained does not, however, represent an actual dispersion period or position of metallic reflexion as it is too small to account for the natural dispersion. The mean dispersional period for the latter required by formula (3) is placed by Martens at $\cdot2175$, and by Flatow at $\cdot2255$. The formulæ obtained, however, do not fit at all well in the extreme ultraviolet, *e. g.*,

λ.	n(obs.) (Flatow).	Diff. (Martens).	Diff. (Flatow).
$\cdot274$	$2\cdot0053$	$-\cdot0073$	$+\cdot0320$

As the errors are of opposite sign it is probable that the mean band lies between the two values here given. The low value obtained from the magnetic rotation shows that the constant k_2 must be introduced, as in equation (10), but this equation cannot be applied to calculate the longer dispersional period without a more extended series of observations or measurements carried to a higher degree of accuracy in the visible. I hope to repeat the determination shortly with a more powerful electromagnet.

Symmetrical Units.—The system of units adopted in the formulæ above is that in which all electrical quantities, including current and resistance, are expressed in electrostatic units, all magnetic quantities in electromagnetic units, the connexion between the two being established by the two circuital relations :

$$\frac{4\pi}{C} \frac{d\mathrm{P}}{dt} = \operatorname{curl} \mathrm{H},$$

$$\frac{1}{C} \frac{d\mathrm{B}}{dt} = \operatorname{curl} \mathrm{X}.$$

This system, which is that adopted by Lorentz in his 'Theory of Electrons' (in which, however, Heaviside's rational values are used), appears to be the best adapted to the interpretation of experimental results.

Summary.

(1) The calculation of ultraviolet free-periods from ordinary dispersion leads in general to a mean effective value only. New formulæ are obtained for benzene, m. xylene, and α-monobromnaphthalene.

(2) When a similar calculation is made from magnetic rotary dispersion using the formula

$$\phi = k\left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2}\right)^2,$$

the value obtained is usually much shorter and often progressive. As the latter formula contains no *adjustable* constants, this result shows that in the case of the liquids here examined Meyer's formula does not apply.

(3) When a progressive result is obtained in (2) a close approximation to the longest dispersion period in the ultra-violet can usually be obtained from

$$\phi = k_1\left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2}\right)^2 + k_2.$$

This appears to be due to a much sharper differentiation in the effects of bands of decreasing wave-length in the magnetic case.

(4) In the case of benzene, and possibly also in m. xylene, the longest period is almost an exact submultiple of the period of one of the infra-red bands.
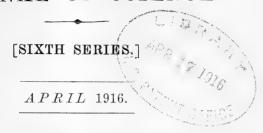
XXXII. *Note on Experiments to detect Refraction of X-rays.*
By CHARLES G. BARKLA, *F.R.S.*[*]

ON the simple theory of dispersion the refractive index
(μ) of a substance is given by an expression of the
form

$$\mu^2 = 1 + \Sigma \frac{Ne^2}{\pi m(n_0^2 - n^2)},$$

where N is the number, per unit volume, of particles of
mass m, charge e, and vibration frequency n_0, and n is the
frequency of the incident radiation. As the frequency of
incident radiation changes from n, that for luminous radiation,
to n', for penetrating X-radiation, each "infra-red term" is
diminished approximately in the ratio n^2/n'^2, and each "ultra-
violet term" (including "M," "L," and "K" characteristic
X-radiation terms) in the ratio $-n_0^2/n'^2$. But if this fre-
quency n' be higher than that of the natural vibration of any
of the constituent electrons, all these terms

$$\frac{Ne^2}{\pi m(n_0^2 - n'^2)}$$

become negative, that is, all the vibrating systems affect the
refractive index in the same way.

If then the theory were applicable even in a modified
form to radiation of such short wave-length as that in
Röntgen radiation, it seemed just possible that by careful
experiment refraction might in certain cases be detected.

[*] Communicated by the Author.

Experiments had previously been made on the same subject by a number of investigators, but they had not been of such a kind as with our present state of knowledge to justify any hope of success.

The refracting surfaces were usually ordinary optical surfaces, in which the irregularities were in general large compared with the wave-length of Röntgen radiation. This being the case, any refraction occurring would be irregular refraction which would produce only a certain amount of diffusion in a transmitted pencil and consequent blurring of the " image." The methods of detection, too, were not the most sensitive.

In the following experiments a prism of large angle and with crystalline refracting surface was used ; the pencil of radiation transmitted was an exceedingly narrow one ; the experimental arrangement was such as to make a small deviation measurable ; and the material of the refracting prism and the transmitted radiation in certain cases were such that the frequency of the latter was not far removed from the natural frequency of vibration of one set of electrons in the other.

The refracting substances used in these experiments were rock-salt and potassium bromide, the two refracting surfaces being crystalline planes at right angles. A narrow pencil of X-radiation was passed through the refracting right-angled prism and was received on a photographic plate on the other side.
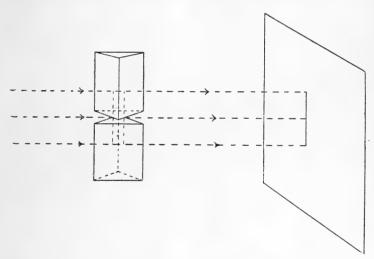
In the initial experiments the X-radiation was sent through two parallel slits in parallel lead screens. In the path of this pencil beyond the second slit was placed the prism with its refracting edge parallel to the slits but intercepting only one-half of the beam. Thus, of the very narrow pencil, one-half * passed through the air just outside the prism, while the other passed through the prism. At first curious effects were produced on the photographic plate beyond, some of which were suggestive of refraction : the two portions of the beam were apparently separated, for a clear line appeared between the two dark "images" on the negative. It was, however, found that such effects, and fringe effects observed at the edge of a shadow, were due to (1) the finite magnitude of the source, and (2) the lack of proportionality between the density of a photographic image and the intensity of the radiation producing it.

These results led to nothing fundamentally new ; they are

* Of half the *width*.

only worth mentioning as of a kind likely to lead to wrong interpretation.

The final experiments are, however, probably worth recording. The radiation from an X-ray tube passed successively through two narrow vertical slits in parallel lead screens about 50 centimetres apart, on to a photographic plate at a distance of about 150 centimetres from the second screen. The photographic impression produced by the pencil of radiation was then a thin vertical line 3 centimetres long and about ·01 centimetre in width. A few centimetres away from the second lead screen were placed two crystals of potassium bromide arranged as two refracting prisms end to end—that is, one above the other—with refracting edges vertical but with their bases on opposite sides of the transmitted radiation

(see figure). Thus any refraction of the radiation in transmission through the prisms would result in displacements in opposite directions of the upper and lower halves of the thin pencil of radiation. An exposure of a rapid plate was made for a period of from five to eight hours. It was found that the photographic impression was still a straight line from top to bottom. There was no evidence of the slightest break or lateral separation between the two halves of the image. When looking at the line image in a direction making a small angle with its length, it was estimated that a relative lateral displacement of ·025 millimetre could have been detected.

Thus the transmission through the crystal had not produced a deflexion of ·012 millimetre at a distance of 140 (about) centimetres from the refracting prism ; that is, the deviation was less than 2 seconds of arc. We conclude from this that the refractive index of potassium bromide for radiation of wave-length in the neighbourhood of ·5 × 10⁻⁸ cm. is between 0·999995 and 1·000005 *.

It is of course possible that if only radiation of frequency within certain narrow limits were refracted appreciably, the intensity of this would be too small to produce a distinguishable feature on the photographic plate.

Experiments with more nearly homogeneous beams of radiation might indicate such refraction for a particular wave-length. Although this is a possibility, there is little reason for expecting that such experiments would lead to results differing from those already obtained. For the radiations used in these experiments covered a great portion of what may be regarded as the K absorption band associated with the bromine " K " radiation.

I wish to express my thanks to Mr. J. H. Hagger,— now Inspector of Munitions—for his assistance in these experiments.

XXXIII. *On the Constitution of the Surface Layers of Liquids. By* S. A. SHORTER, *D.Sc., Assistant Lecturer in Physics in the University of Leeds.*—Part I. †

§ 1. *Introduction.*

THE principles of thermodynamics were first applied to the question of the constitution of the heterogeneous layer separating two phases, by Gibbs in his well-known work " On the Equilibrium of Heterogeneous Substances " ‡. As in the case of many other extremely interesting problems, Gibbs's mode of treatment of the subject presents mathematical difficulties, which are insuperable to practically all of those to whom the subject is of interest. The object of

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* Bromine K radiation has a wave-length about 10⁻⁸ cm.
† Communicated by the Author.
‡ Scientific Papers, vol. i. p. 235.

the present work is to develop the thermodynamical theory of the subject in an elementary manner, preserving at the same time perfect mathematical rigour and the utmost generality of treatment.

The first attempt at an elementary exposition of the subject was made by Milner *, who obtained a formula for the "surface excess" of a solute, applicable to the case of a dilute solution in contact with a third substance.

The theory developed in the present work is applicable to solutions of any degree of concentration—and therefore to the case of a mixture of two perfectly miscible liquids. Since in this latter case the distinction between solvent and solute is a purely arbitrary one, the theory must take account of the "surface excess" of both solvent and solute. This consideration of the "surface excess" of both components of a solution leads to a curious and interesting principle, which I have termed the "Principle of the Relativity of the Surface Magnitudes." This principle underlies all Gibbs's theory, though it is never explicitly referred to in it.

§ 2. *The General Case of a Binary System.*

We will first consider the case of the interface separating two phases of a system containing two components. This general case includes a number of special cases, which we will consider in § 4 of the present paper.
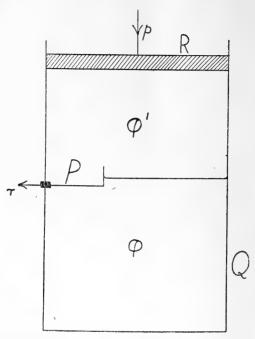
The most elementary method of treating the subject is to consider the working of an ideal "engine" in which the contractile tendency of the surface and the expansive tendency of the volume are both used as a means of producing an external mechanical effect. Such an engine is represented in fig. 1. Q is a vessel of rectangular horizontal cross-section, containing masses M_0 and M_1 of two components C_0 and C_1 respectively, in two phases ϕ and ϕ' separated by a plane surface of area σ and tension τ. The area of the surface may be varied by means of a movable plate P, which fits accurately to the sides of the vessel parallel to the plane of the paper. The horizontal portion of this plate passes through a slot in one of the vertical sides perpendicular to the plane of the paper. This side is sufficiently thick in the neighbourhood of the slot for the plate to be incapable of any motion but a horizontal motion of translation. The volume v of the system may be varied by means of the piston R.

* Phil. Mag. Jan. 1907.

Suppose now that the engine goes through a reversible isothermal cycle. According to the first law of thermodynamics, the total work done by the system is equal to the

Fig. 1.

total heat absorbed by it. According to the second law the total heat absorbed is zero. Hence the total work done is zero.

Let the cycle consist of the following four stages :—

(1) The surface-tension being maintained at the constant value τ, let the volume v of the system be changed till the surface increases from σ to $\sigma + \delta\sigma$. During this change the pressure p will remain constant.

(2) The area of the surface being maintained constant, let the pressure p be changed till the surface-tension changes from τ to $\tau + \delta\tau$.

(3) The surface tension being maintained constant, let the volume be changed till the area of the surface changes from $\sigma + \delta\sigma$ to σ.
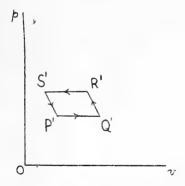
(4) The area of the surface being maintained constant, let the pressure be changed till the surface-tension changes from $\tau + \delta\tau$ to τ.

If we take values of σ as abscissæ and values of τ as ordinates, the cycle is represented by the elementary rectangle PQRS of area $\delta\sigma\delta\tau$, described in an anti-clockwise

Fig. 2.

direction (see fig. 2). Hence the system does an amount of work $\delta\sigma\delta\tau$ *against* the force controlling the surface *. The force controlling the volume must therefore do an equal amount of work *on* the system. Suppose now that we take

Fig. 3.

values of v as abscissæ and values of p as ordinates. The cycle will be represented by a parallelogram $P'Q'R'S'$ (see fig. 3) with two sides ($P'Q'$ and $R'S'$) parallel to the v axis,

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* A certain force will be necessary to counteract the effect of the difference in the hydrostatic pressure on the two sides of the vertical portion of the plate P. Since the work done by this force in any displacement is equal to the product of the total weight of the components and the increase in the height of their centre of gravity, the work done in a cycle will be zero, so that this force may be left out of account in considering a cycle of operations.

of length $(dv/d\sigma)_{\theta\tau}\delta\sigma$, a distance $(dp/d\tau)_\theta\delta\tau$ apart. Now the perimeter must be described in an anti-clockwise direction. Hence the above two differential coefficients must have the same sign; so that equating the areas of the parallelograms PQRS and P'Q'R'S', we obtain the relation

$$\left(\frac{dv}{d\sigma}\right)_{\theta\tau} = \left(\frac{d\tau}{dp}\right)_\theta. \quad \cdots \quad (1)$$

Since in a binary system the constancy of τ and θ is equivalent to the constancy of p and θ, this equation may be written *

$$\left(\frac{dv}{d\sigma}\right)_{p\theta} = \left(\frac{d\tau}{dp}\right)_\theta. \quad \cdots \quad (2)$$

We see from this equation that if the surface-tension depends upon the pressure, it is necessary to change the volume, when the area of the surface is changed, in order to keep unchanged the nature of the different parts of the system. Such a change would obviously be unnecessary if the two phases were homogeneous right up to the surface of separation. Let ρ_0 and ρ_1 denote the densities in the ϕ phase, and ρ_0' and ρ_1' those in the ϕ' phase, of C_0 and C_1 respectively. Let V and V' denote the respective volumes of the phases, and M_0 and M_1 the respective total masses of the components. We see that in general the equations

$$M_0 = \rho_0 V + \rho_0' V',$$
$$M_1 = \rho_1 V + \rho_1' V',$$

will not be verified. Let us write

$$\sigma\Gamma_0 = M_0 - (\rho_0 V + \rho_0' V'), \quad \cdots \quad (3)$$
$$\sigma\Gamma_1 = M_1 - (\rho_1 V + \rho_1' V'). \quad \cdots \quad (4)$$

We will call (following Milner †) each of the quantities Γ_0 and Γ_1 (defined by the above equations) the "surface excess" of the corresponding component. It is evident that Γ_0 and Γ_1 will depend only on the nature of the system, and not on the dimensions of its parts.

The differential coefficient $(dv/d\sigma)_{\theta p}$ is easily evaluated in

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* This relation may be deduced more concisely, though in a less elementary manner, from the equation $dU = \theta dS - p\,dv + \tau\,d\sigma$ (U = energy, S = entropy), by writing it in the form $d(U - \theta S + pv) = -S\,d\theta + v\,dp + \tau\,d\sigma$.
† *Loc. cit.* Gibbs uses the term "surface density."

terms of Γ_0, Γ_1 and the densities. Since the constancy of p and θ involves the constancy of ρ_0, ρ_0', ρ_1, ρ_1', Γ_0 and Γ_1, we have from equations (3) and (4)

$$\Gamma_0 d\sigma + \rho_0 dV + \rho_0' dV' = 0 \quad \cdots \quad (5)$$

and

$$\Gamma_1 d\sigma + \rho_1 dV + \rho_1' dV' = 0. \quad \cdots \quad (6)$$

Since

$$v = V + V' \quad \cdots \quad \cdots \quad (7)$$

we have

$$dv = dV + dV'. \quad \cdots \quad \cdots \quad (8)$$

From equations (5), (6), and (8) we readily obtain the desired relation

$$\left(\frac{dv}{d\sigma}\right)_{\theta p} = \frac{\Gamma_1(\rho_0 - \rho_0') - \Gamma_0(\rho_1 - \rho_1')}{\rho_0' \rho_1 - \rho_0 \rho_1'} \quad \cdots \quad (9)$$

Substituting this value in equation (2) we obtain the equation

$$\frac{\Gamma_1}{\rho_1 - \rho_1'} - \frac{\Gamma_0}{\rho_0 - \rho_0'} = \frac{\rho_0' \rho_1 - \rho_0 \rho_1'}{(\rho_0 - \rho_0')(\rho_1 - \rho_1')}\left(\frac{d\tau}{dp}\right)_\theta . \quad (10)$$

This is the most general relation possible (in the case of a binary system) between the surface magnitudes and quantities capable of experimental determination.
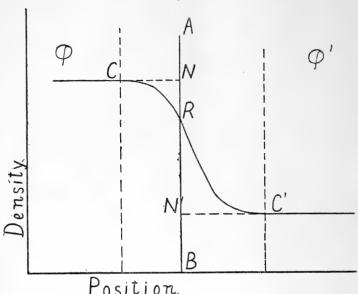
§ 3. *The Principle of the Relativity of the Surface Magnitudes.*

It will be seen that in the case of a binary system our theory gives only one equation connecting the two quantities Γ_0 and Γ_1 with quantities capable of experimental determination. We cannot obtain separate equations for Γ_0 and Γ_1. At first sight, this seems to imply some incompleteness or imperfection in the thermodynamical theory. A closer examination of what is meant by the term "surface excess" shows, however, that this idea is wrong, and that the theory yields all that could be expected of it.

Suppose that we take as abscissæ the distances of points from some reference plane parallel to the surface, and as ordinates the values of the density of a component. The graph will consist of two straight lines parallel to the axis of abscissæ (corresponding to the interiors of the two phases) joined by a curved line (corresponding to the region of

heterogeneity). A simple type of such a curve is shown in
fig. 4. It is evident that the position of the surface of

Fig. 4.

Position.

separation may be assigned quite arbitrarily within the limits
of the region of heterogeneity. If we assign a position AB,
the surface excess is given by

$$\Gamma = \text{area } C'N'R - \text{area } CNR.$$

The value of Γ may vary within wide limits with the
arbitrarily assigned position of the surface of separation.

If we choose the position of AB so that

$$\text{area } CNR = \text{area } C'N'R,$$

the surface excess is zero. We will call the plane, relative
to which the surface excess of a component is zero, the
"zero-plane" of that component. If the density assumes in
the surface-layer values greater than in either phase, the
position of the "zero-plane" is fixed (see fig. 5) by the
relation

$$\text{area } CED + \text{area } C'N'R = \text{area } RDN.$$

If the increase in density in the surface-layer is very great
the "zero-plane" may lie in the interior of one of the phases
(as in fig. 6).

Fig. 5.
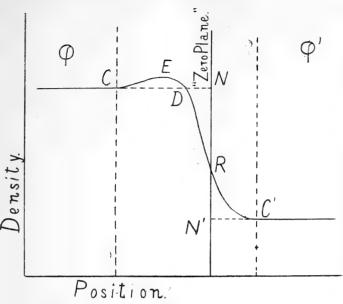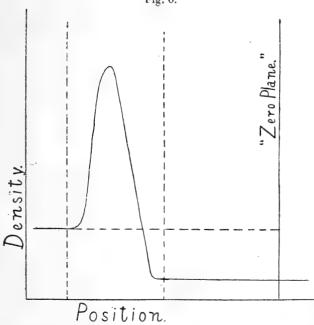
Fig. 6.

The value of the surface excess relative to a plane a distance z from the "zero-plane" in the direction of the ϕ phase is evidently given by

$$\Gamma = (\rho - \rho')z.$$

Consider now a system of two components C_0 and C_1. The "zero-plane" of each component will have a definite position, and the distance between the two will have a definite value, characteristic of the system. Suppose now that Γ_0 and Γ_1 are the respective values of the surface excesses, relative to a plane whose distances from the "zero-planes" of C_0 and C_1, measured in the direction of the ϕ phase, are z_0 and z_1 respectively. We then have

$$\Gamma_0 = (\rho_0 - \rho_0')z_0$$

and

$$\Gamma_1 = (\rho_1 - \rho_1')z_1.$$

Hence, if h denote the distance of the "zero-plane" of C_1 from that of C_0 measured in the direction of the ϕ' phase, we have

$$h = z_1 - z_0 = \frac{\Gamma_1}{\rho_1 - \rho_1'} - \frac{\Gamma_0}{\rho_0 - \rho_0'}.$$

Referring back to equation (10)—the general equation for a binary system—we see at once the reason for the apparent incompleteness of our theory and the particular form of the equation. The quantities Γ_0 and Γ_1 are purely arbitrary magnitudes which could not possibly appear singly in any thermodynamical relation. They may, however, be combined in such a way as to yield a quantity which is not arbitrary, and this quantity appears on the left-hand side of equation (10), which may be written in the form

$$h = \frac{\rho_0'\rho_1 - \rho_0\rho_1'}{(\rho_0 - \rho_0')(\rho_0 - \rho_1')}\left(\frac{d\tau}{dp}\right)_\theta. \quad . \quad . \quad . \quad (11)$$

We may, however, interpret equation (10) in another way. The value of the surface excess of C_1 relative to the "zero-plane" of C_0 is evidently $(\rho_1 - \rho_1')h$ or

$$\Gamma_1 - \frac{\rho_1 - \rho_1'}{\rho_0 - \rho_0'}\Gamma_0.$$

Let us adopt the notation of Gibbs and use the symbol

$\Gamma_{r(s)}$ to denote the surface excess of any component C_r in a system relative to the "zero-plane" of another component C_s. Equation (10) may then be written

$$\Gamma_{1(0)} = \frac{\rho_0{'}\rho_1 - \rho_0\rho_1{'}}{\rho_0 - \rho_0{'}}\left(\frac{d\tau}{dp}\right)_\theta . \quad . \quad . \quad . \quad . \quad (12)$$

The value of the surface excess of C_0 relative to the "zero-plane" of C_1 is evidently equal to $-(\rho_0 - \rho_0{'})h$ or

$$\Gamma_0 - \frac{\rho_0 - \rho_0{'}}{\rho_1 - \rho_1{'}}\Gamma_1,$$

so that equation (10) may be written

$$\Gamma_{0(1)} = -\frac{\rho_0{'}\rho_1 - \rho_0\rho_1{'}}{\rho_1 - \rho_1{'}}\left(\frac{d\tau}{dp}\right)_\theta . \quad . \quad . \quad . \quad (13)$$

The above general considerations apply, of course, to a system containing any number of components. Thus in the case of a system of n components, there are n "zero-planes," and the theory should yield $n-1$ equations for the $n-1$ lengths which fix the relative positions of these planes.

In recent years the surface excess of a solute in a binary liquid mixture has been determined experimentally by observing the change of concentration caused by a large extension of surface. We have seen that the surface excess of a component is a purely arbitrary magnitude, so that the interesting question arises as to what is given by the above experiment. The only case which has been investigated practically is that of a solution in contact with a third substance. This case will be considered in Part II. of the present work. We will consider here an imaginary experiment with a two-phase binary system, which could not be realized in practice because of the smallness of the changes involved, but which will serve to illustrate the point in question. Suppose that a closed vessel contains a binary liquid mixture in contact with the vapour phase. Let the vessel be tilted so that the area of the surface separating the phases is increased from σ to $\sigma + \Delta\sigma$. This will in general cause the vapour pressure to alter. Suppose that by the addition of an amount ΔM_1 of the solute C_1 the initial pressure (and therefore the initial concentration of the solution) is restored. One would at once say that the surface excess of the solute is $\Delta M_1/\Delta\sigma$. Let us examine

the question in the light of the above theory. Initially we have

$$M_0 = \rho_0 V + \rho_0' V' + \Gamma_0 \sigma,$$

$$M_1 = \rho_1 V + \rho_1' V' + \Gamma_1 \sigma,$$

and, finally,

$$M_0 = \rho_0(V + \Delta V) + \rho_0'(V' + \Delta V') + \Gamma_0(\sigma + \Delta \sigma),$$

$$M_1 + \Delta M_1 = \rho_1(V + \Delta V) + \rho_1'(V' + \Delta V') + \Gamma_1(\sigma + \Delta \sigma) ;$$

and since the total volume is constant

$$\Delta V + \Delta V' = 0.$$

From these equations we readily find that

$$\frac{\Delta M_1}{\Delta \sigma} = \Gamma_1 - \frac{\rho_1 - \rho_1'}{\rho_0 - \rho_0'} \Gamma_0 = \Gamma_{1(0)}, \quad . \quad . \quad (14)$$

i. e. that the value of the surface excess of C_1 deduced from the experimental data is the value relative to the "zero-plane" of C_0.

§ 4. *Special Cases of a Binary System.*

Case I. Two Immiscible Liquids.

The simplest case of a binary system is that in which each phase consists of a single substance, *i. e.* that formed by two immiscible liquids. Let us suppose that the ϕ phase contains only the component C_0, and the ϕ' phase only the component C_1. Equation (10) then takes the form

$$\frac{\Gamma_1}{\rho_1'} + \frac{\Gamma_0}{\rho_0} = -\left(\frac{d\tau}{dp}\right)_\theta. \quad . \quad . \quad . \quad (15)$$
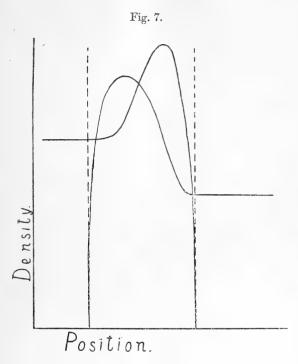
This equation may also be written in the forms

$$\Gamma_{1(0)} = -\rho_1\left(\frac{d\tau}{dp}\right)_\theta \quad . \quad . \quad . \quad . \quad (16)$$

and

$$\Gamma_{0(1)} = -\rho_0\left(\frac{d\tau}{dp}\right)_\theta. \quad . \quad . \quad . \quad (17)$$

This result is of importance in relation to the question of the composition of the surface-layers of pure liquids. It is

often asserted that the surface-layers of a liquid are in a state of compression *. According to Lewis †, who has developed a quantitative theory of this supposed surface compression, the variation of the densities of two immiscible liquids in the neighbourhood of the surface

Fig. 7.

separating them is as shown in fig. 7. In the case of water it is calculated that the mean density in the surface-layer is about twice that in the body of the liquid. An effect of the same order of magnitude is calculated for a number of other liquids. In the exceptional case of mercury the mean density in the surface-layer is only ·84 of the bulk density.

Let us examine this theory of surface compression in the

* See, for example, 'The Chemistry of Colloids,' by W. W. Taylor (Arnold, 1915), pp. 229 & 250.
† Phil. Mag. Sept. 1910, p. 502 ; *Kolloid-Zeitschrift*, vol. vii. p. 197 (1910).

light of the thermodynamical theory given above.   Equation (15) may be written in the form

$$h = \left(\frac{d\tau}{dp}\right)_\theta \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (18)$$

where h, it will be remembered, is the distance of the "zero-plane" of C_1 from that of C_0 measured in the direction of the ϕ' phase.   Now in the case of a system having a density diagram of the kind shown in fig. 7, h is evidently negative—as is also the case if only one of the liquids exhibits surface compression.   Hence the theory of surface compression leads to the conclusion that the tension of the interface separating two immiscible liquids is diminished by increase of pressure.   This result may, of course, be deduced from quite elementary considerations.   The change of pressure produced by an extension of the interface at constant volume must be such as to increase the tension.   If the liquids are compressed in the surface-layers this extension produces a diminution of pressure so that $d\tau/dp$ is negative.

The effect of pressure on the interfacial tension has been investigated by Lynde [*] in the case of a number of pairs of immiscible or partially miscible liquids.   In the case of water and mercury it is found that the interfacial tension is increased ·74 per cent. by an increase of pressure of 5000 lb. per sq. inch.   This gives (assuming $\tau = 370$ dyne/cm.) for $d\tau/dp$ the value $8·2 \times 10^{-9}$ cm. or ·082 $\mu\mu$.

This result is, of course, inconsistent with the view that either the water or the mercury are compressed in the surface-layer.   It is interesting to calculate the order of magnitude of $d\tau/dp$ required by Lewis's theory.   Since the mercury does not suffer any superficial increase of density its "zero-plane" will be situated somewhere in the surface-layer.   Since the mean density of the water in the surface-layer is double the bulk density, the "zero-plane" of the water will lie in the interior of the mercury, a distance from the nearer boundary of the surface-layer equal to the thickness of the surface-layer.   We therefore have

$$- \frac{d\tau}{dp} > \text{thickness of surface-layer.}$$

If we assume the value 10^{-6} cm. for the thickness of the

surface-layer, we obtain a value of $d\tau/dp$ opposite in sign to, and arithmetically more than a hundred times as large as, the value obtained experimentally.

A similar discrepancy between theory and experiment exists in the case of the ether-mercury interface, Lynde's experiments giving for $d\tau/dp$ a small positive value, and Lewis's theory a relatively large negative value. Our theory shows, therefore, that the theory of surface compression is inconsistent with experimental data relating to the effect of pressure on the interfacial tension.

Case II. Two Partially Miscible Liquids.

Suppose that the two phases are the liquid layers formed by two partially miscible liquids, the ϕ phase being the C_0 layer. If we write $c_0 = \rho_0'/\rho_0$ and $c_1 = \rho_1/\rho_1'$, we have

$$\Gamma_{1(0)} = -\frac{\rho_1'(1 - c_0 c_1)}{1 - c_0}\left(\frac{d\tau}{dp}\right)_\theta . \quad . \quad . \quad . \quad (19)$$

or

$$h = \frac{1 - c_0 c_1}{(1 - c_0)(1 - c_1)}\left(\frac{d\tau}{dp}\right)_\theta . \quad . \quad . \quad . \quad (20)$$

Lynde's results for three pairs of partially miscible liquids, together with the calculated values of h, $\Gamma_{0(1)}$, and $\Gamma_{1(0)}$ are shown in the following table.

C_0.	C_1.	τ in dyne/cm.	$\dfrac{d\tau}{dp}$ in $\mu\mu$.	h in $\mu\mu$.	$\Gamma_{0(1)}$ in 10^{-8} gm./cm.^{2}	$\Gamma_{1(0)}$ in 10^{-8} gm./cm.^{2}
Water.	Ether.	9·7	−·060	−·068	+·6	+·4
Water.	Chloroform.	27	−·006	−·006	+·06	+·09
Water.	Carbon bisulphide.	42	+·037	+·041	−·4	−·5

It will be seen that in two cases $d\tau/dp$ is negative. The distance between the "zero-planes" is, however, much too small to justify any assumption of surface compression.

Case III. Liquid Phase in contact with Vapour Phase (both components volatile).

In this case we may in general neglect the densities in the vapour phase in comparison with those in the liquid phase.

Equation (10) then becomes

$$\frac{\Gamma_1}{\rho_1} - \frac{\Gamma_0}{\rho_0} = \left(\frac{\rho_0'}{\rho_0} - \frac{\rho_1'}{\rho_1}\right)\left(\frac{d\tau}{dp}\right)_\theta. \quad . \quad . \quad . \quad (21)$$

or

$$\Gamma_{1(0)} = \left(\frac{\rho_1\rho_0'}{\rho_0} - \rho_1'\right)\left(\frac{d\tau}{dp}\right)_\theta. \quad . \quad . \quad . \quad (22)$$

If we suppose the vapour phase to consist of an ideal mixture of gases of molecular weights m_0 and m_1 respectively, the above equation reduces to

$$\Gamma_{1(0)} = \frac{\rho_1}{R\theta}\left(\frac{m_0 p_0}{\rho_0} - \frac{m_1 p_1}{\rho_1}\right)\left(\frac{d\tau}{dp}\right)_\theta, \quad . \quad . \quad (23)$$

where R is the "gas constant," and p_0 and p_1 the partial pressures of the vapours of C_0 and C_1 respectively. If we suppose the state of the system to be specified by the concentration c of the solution of C_1 in C_0 we may write

$$\Gamma_{1(0)} = \frac{\rho_1}{R\theta}\left(\frac{m_0 p_0}{\rho_0} - \frac{m_1 p_1}{\rho_1}\right)\frac{\left(\frac{d\tau}{dc}\right)_\theta}{\left(\frac{dp}{dc}\right)_\theta}. \quad . \quad . \quad (24)$$

The concentration c may be defined in any of the three usual ways

$$c = \rho_1,$$

$$c = \frac{\rho_1}{\rho_0},$$

and

$$c = \frac{\rho_1}{\rho_0 + \rho_1}.$$

Let us now consider the case of an ideal dilute solution of C_1 in C_0. In such a solution the partial pressure of the solute is proportional to its concentration, and the relative lowering of the pressure of the solvent is equal to the "molar fraction" of the solute. We have therefore

$$p_1 = K\rho_1, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where K is some constant * about the magnitude of which

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* Or more precisely, some function of the temperature.

the Theory of the Ideal Dilute Solution makes no statement; and

$$\frac{P_0 - p_0}{P_0} = \frac{m_0 \rho_1}{m_1 \rho_0}, \quad \cdots \quad (26)$$

where P_0 is the vapour-pressure of the pure solvent. Substituting the values of p_0, p_1, and dp given by equations (25) and (26) in equation (23) we obtain the result

$$\Gamma_{1(0)} = -\frac{m_1 \rho_1}{R\theta} \left(\frac{d\tau}{d\rho_1}\right)_\theta, \quad \cdots \quad (27)$$

which differs from the well-known result deduced by Milner * only in respect to the more precise definition of the "surface excess." We thus see that the equation applies to the case of a dilute solution of a volatile substance in contact with the vapour phase.

We will consider the question of liquid mixtures in Part II., when we deal with the case of a solution in contact with a third substance. Practically all the experimental data available for illustrating the theory relate to this latter case, which is a special case of a ternary system.

Case IV. Liquid Phase in contact with Vapour Phase (only one component volatile).

If C_1 is involatile equation (22) becomes

$$\Gamma_{1(0)} = \frac{\rho_1 \rho_0'}{\rho_0} \left(\frac{d\tau}{dp}\right)_\theta. \quad \cdots \quad (28)$$

If the solvent vapour behaves as an ideal gas of molecular weight m_0, we have

$$\Gamma_{1(0)} = \frac{m_0 \rho_1 p}{R\theta} \left(\frac{d\tau}{dp}\right)_\theta. \quad \cdots \quad (29)$$

In the case of an ideal dilute solution equation (27) is obviously valid.

The University of Leeds.
    Feb. 3rd, 1916.

* *Loc. cit.*

XXXIV. *On a Method for deriving Mutual- and Self-Inductance Series. By* S. Butterworth, *M.Sc., Lecturer in Physics, School of Technology, Manchester* [*].

1. NUMEROUS series formulæ have been obtained for the mutual induction between coaxial circles [†]. In general, these formulæ have been completely determined (*i.e.* the range of convergency and general term are known) only in the case of circles far apart.

It is proposed in the present paper to develop a method which will yield the general term for formulæ which hold when the circles are close together.

2. Let the radii of the circles be A and a, and let b be the distance of their centres. Then the mutual induction between them is given by the Elliptic Integral formula [‡]

$$\mathrm{M} = 4\pi \sqrt{\mathrm{A}a} \left\{ \left(\frac{2}{k} - k \right) \mathrm{K} - \frac{2}{k} \mathrm{E} \right\}, \quad . \quad . \quad (1)$$

in which

$$k^2 = \frac{4\mathrm{A}a}{(\mathrm{A}+a)^2 + b^2}$$

and K and E are complete Elliptic Integrals of the first and second kind respectively with k as modulus.

By differentiating (1) twice with respect to k, remembering that

$$\frac{d\mathrm{E}}{dk} = \frac{\mathrm{E} - \mathrm{K}}{k}, \qquad \frac{d\mathrm{K}}{dk} = \frac{\mathrm{E}}{k(1-k^2)} - \frac{\mathrm{K}}{k},$$

to obtain expressions for $\frac{d\mathrm{M}}{dk}$ and $\frac{d^2\mathrm{M}}{dk^2}$, and eliminating E and K between these expressions and (1), we find that

$$k^2(1-k^2)\frac{d^2\mathrm{M}}{dk^2} - k(1+k^2)\frac{d\mathrm{M}}{dk} - 3\mathrm{M} = 0. \quad . \quad . \quad (2)$$

By the substitutions $\mathrm{M} = k^3 y$, $k^2 = x$, (2) transforms into

$$\vartheta(\vartheta+2)y = x(\vartheta + \tfrac{3}{2})^2 y, \quad . \quad . \quad . \quad . \quad (3)$$

in which $\vartheta \equiv x\dfrac{d}{dx}$.

This equation is of the type

$$\vartheta(\vartheta+\gamma-1)y = x(\vartheta+\alpha)(\vartheta+\beta)y, \quad . \quad . \quad . \quad (4)$$

the equation of the hypergeometric series, so that, employing the usual transformations for this type, we obtain as equivalent forms of (3)

$$\vartheta_1^2 y_1 = x_1(\vartheta_1+\tfrac{3}{2})^2 y_1 \quad . \quad . \quad . \quad . \quad (3\,a)$$

$$\vartheta_2^2 y_2 = x_2(\vartheta_1-\tfrac{1}{2})^2 y_2 \quad . \quad . \quad . \quad . \quad (3\,b)$$

$$\vartheta_3(\vartheta_3+2)y_3 = x_3(\vartheta_3+\tfrac{3}{2})^2 y_3 \quad . \quad . \quad . \quad . \quad (3\,c)$$

$$\vartheta_4^2 y_4 = x_4(\vartheta_4+\tfrac{3}{2})(\vartheta_4-\tfrac{1}{2})y_4, \quad . \quad . \quad (3\,d)$$

in which

$$y_1 = y, \qquad y_2 = x^2 y, \qquad y_3 = (1-x)^{\tfrac{3}{2}}y, \quad y_4 = x^3 y,$$

$$x_1 = 1-x, \quad x_2 = 1-x, \quad x_3 = \frac{x}{x-1}, \qquad x_4 = \frac{x-1}{x},$$

and

$$\vartheta_n \equiv x_n \frac{d}{dx_n}.$$

3. In forming the primitives of equation (3), it must be noted that γ is, in all cases, a positive integer, so that the usual second particular solution of (4), viz.,

$$y = x^{1-\gamma} F(\alpha+\gamma-1, \ \beta+\gamma-1, \ 2-\gamma, \ x),$$

is no longer valid. However, when γ is a negative integer, the complete primitive of (4) may be obtained as follows :—
Denote by $G(\alpha, \beta, \gamma, \delta, x)$ the series

$$1 + \frac{\alpha\beta}{\gamma\delta}x + \frac{\alpha(\alpha+1)\beta(\beta+1)}{\gamma(\gamma+1)\delta(\delta+1)}x^2 + \dots.$$

and apply the operator

$$\mu = \vartheta(\vartheta+\gamma-1) - x(\vartheta+\alpha)(\vartheta+\beta)$$

to $\quad y = \lambda x^\lambda G(\alpha+\lambda, \ \beta+\lambda, \ \gamma+\lambda, \ 1+\lambda, \ x).$

Then $\mu(y) = \lambda^2(\lambda+\gamma-1)x^\lambda$

and $\mu\left(\dfrac{\partial y}{\partial \lambda}\right) = \lambda(3\lambda+2\gamma-2)x^\lambda + \lambda^2(\lambda+\gamma-1)x^\lambda \log_e x,$

so that $\quad \mathrm{lt}_{\lambda=0}\, \mu\left\{\left(A + B\dfrac{\partial}{\partial \lambda}\right)y\right\} = 0,$

or a possible solution of (4) is

$$y = \mathrm{lt}_{\lambda=0}\left(A + B\frac{\partial}{\partial\lambda}\right)\{\lambda x^{\lambda} G(\alpha+\lambda,\ \beta+\lambda,\ \gamma+\lambda,\ 1+\lambda,\ x)\}. \qquad \qquad (5)$$

When γ is anything but a negative integer or zero (5) reduces to

$$y = BF(\alpha,\ \beta,\ \gamma,\ x),$$

the usual first solution of (4), but when γ is a negative integer (say $-n$), all the terms in

$$G(\alpha+\lambda,\ \beta+\lambda,\ \gamma+\lambda,\ 1+\lambda,\ x)$$

beyond the $(n+1)$st contain λ as a factor in the denominator, so that both the particular solutions implied in (5) will remain finite when λ vanishes. Hence, in this case (5) yields the complete primitive.

Moreover, if γ is a positive integer greater than unity, the substitution $y = ux^{1-\gamma}$ applied to (4) will convert that equation into one of the same type in which the new γ is a negative integer or zero.

Finally, if γ is unity, the complete primitive of (4) is

$$y = \mathrm{lt}_{\lambda=0}\left(A + B\frac{\partial}{\partial\lambda}\right)\{x^{\lambda} G(\alpha+\lambda,\ \beta+\lambda,\ 1+\lambda,\ 1+\lambda,\ x)\}. \qquad \qquad (5a)$$

4. Using (5) and (5 a) to obtain the primitives of (3), we find that

$$\frac{M}{4\pi\sqrt{\bar{A}a}} = \mathrm{lt}_{\lambda=0}x^{\frac{3}{2}}\left(A + B\frac{\partial}{\partial\lambda}\right)\{\lambda x^{\lambda-2} G(\lambda-\tfrac{1}{2},\ \lambda-\tfrac{1}{2},\ \lambda-1,\ \lambda+1,\ x)\} \quad (6)$$

$$= \mathrm{lt}_{\lambda=0}x^{\frac{3}{2}}\left(A_1 + B_1\frac{\partial}{\partial\lambda}\right)\{x_1^{\lambda} G(\lambda+\tfrac{3}{2},\ \lambda+\tfrac{3}{2},\ \lambda+1,\ \lambda+1,\ x_1)\} \quad (6a)$$

$$= \mathrm{lt}_{\lambda=0}x^{-\frac{1}{2}}\left(A_2 + B_2\frac{\partial}{\partial\lambda}\right)\{x_2^{\lambda} G(\lambda-\tfrac{1}{2},\ \lambda-\tfrac{1}{2},\ \lambda+1,\ \lambda+1,\ x_2)\}. \quad (6b)$$

$$= \mathrm{lt}_{\lambda=0}x_3^{\frac{3}{2}}\left(A_3 + B_3\frac{\partial}{\partial\lambda}\right)\{\lambda x_3^{\lambda-2} G(\lambda-\tfrac{1}{2},\ \lambda-\tfrac{1}{2}\ \lambda-1,\ \lambda+1,\ x_3)\} \quad (6c)$$

$$= \mathrm{lt}_{\lambda=0}\left(A_4 + B_4\frac{\partial}{\partial\lambda}\right)\{x_4^{\lambda} G(\lambda+\tfrac{3}{2},\ \lambda-\tfrac{1}{2},\ \lambda+1,\ \lambda+1,\ x_4)\}, \quad (6d)$$

in which the constants A_n, B_n have still to be determined.

Since M, x, x_3 vanish with k, $B = B_3 = 0$.   Also when k is small

$$M/4\pi\sqrt{Aa} = \pi k^3/16 = \pi x^{\frac{3}{2}}/16 = -\pi x_3^{\frac{3}{2}}/16$$

by virtue of (1).

Under the same conditions the right hand members of (6) and (6 c) become

$$A x^{\frac{3}{2}}/32 \quad \text{and} \quad A_3 x_3^{\frac{3}{2}}/32 \text{ respectively.}$$

Hence $$A = -A_3 = 2\pi.$$

Using these values in (6) and (6 c) we find

$$M = \frac{\pi^2}{4}\sqrt{Aa}\, k^3\left(1 + \frac{3^2}{2 \cdot 6}k^2 + \frac{3^2 \cdot 5^2}{2 \cdot 4 \cdot 6 \cdot 8}k^4 + \frac{3^2 \cdot 5^2 \cdot 7^2}{2 \cdot 4 \cdot 6 \cdot 8 \cdot 10}k^6 + \dots\right), \quad \text{(A)}$$

and

$$M = \frac{\pi^2}{4}\sqrt{Aa}\,\mu^3\left(1 - \frac{3^2}{2 \cdot 6}\mu^2 + \frac{3^2 \cdot 5^2}{2 \cdot 4 \cdot 6 \cdot 8}\mu^4 - \frac{3^2 \cdot 5^2 \cdot 7^2}{2 \cdot 4 \cdot 6 \cdot 8 \cdot 10}\mu^6 + \dots\right), \quad \text{(B)}$$

in which $$\mu^2 = \frac{k^2}{1 - k^2} = \frac{4Aa}{(A-a)^2 + b^2}.$$

(A) is valid for all distances of the circles, but converges most rapidly when the circles are far apart. It could readily have been obtained by substituting the usual series for K and E in (1).

(B) converges only if $k^2 < \frac{1}{2}$. When the circles are of equal radius $\mu = 2a/b$, and the series is then identical with one obtained by Havelock [*].

x_1, x_2, x_4 vanish when k is unity, and when either of the independent variables is small (6 a), (6 b), and (6 d) assume the form $A_n + B_n \log x_n$. Under the same conditions with $k'^2 = 1 - k^2$,

$$M/4\pi\sqrt{Aa} = \log\frac{4}{k'} - 2 = \log\frac{4}{\sqrt{x_1}} - 2,$$

$$= \log\frac{4}{\sqrt{x_2}} - 2 = \log\frac{4}{\sqrt{-x_4}} - 2.$$

Therefore

$$A_1 = \log 4 - 2 = A_2, \quad A_4 = \log\frac{4}{i} - 2,$$

$$B_1 = B_2 = B_4 = -\tfrac{1}{2}.$$

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[*] Havelock, Phil. Mag. xv. p. 332 (1908).

Using these values in (6 a), (6 b), and (6 d) we find :—

From (6 a)

$$\frac{M}{4\pi\sqrt{Aa}} = k^3\left(\phi_0 + \frac{3^2}{2^2}k'^2\phi_1 + \frac{3^2 \cdot 5^2}{2^2 \cdot 4^2}k'^4\phi_2 + \ldots\right), \quad (C)$$

in which

$$\phi_0 = \log\frac{4}{k'} - 2$$

$$\phi_1 - \phi_0 = \frac{1}{1} - \frac{2}{3}$$

$$\phi_2 - \phi_1 = \frac{1}{2} - \frac{2}{5}$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$\phi_n - \phi_{n-1} = \frac{1}{n} - \frac{2}{2n+1} = \frac{1}{n(2n+1)}$$

From (6 b)

$$\frac{M}{4\pi\sqrt{Aa}} = \frac{1}{k}\left(\phi_0' + \frac{1^2}{2^2}k'^2\phi_1' + \frac{1^2 \cdot 1^2}{2^2 \cdot 4^2}k'^4\phi_2' + \frac{1^2 \cdot 1^2 \cdot 3^2}{2^2 \cdot 4^2 \cdot 6^2}k'^6\phi_3' + \ldots\right), \quad (D)$$

in which

$$\phi_0' = \log\frac{4}{k'} - 2$$

$$\phi_1' - \phi_0' = \frac{1}{1} + \frac{2}{1}$$

$$\phi_2' - \phi_1' = \frac{1}{2} - \frac{2}{1}$$

$$\phi_3' - \phi_2' = \frac{1}{3} - \frac{2}{3}$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$\phi_n' - \phi_{n-1}' = \frac{1}{n} - \frac{2}{2n-3} = -\frac{3}{n(2n-3)}$$

From (6 d)

$$\frac{M}{4\pi\sqrt{Aa}} = \phi_0'' + \frac{1 \cdot 3}{2^2}\frac{1}{\mu^2}\phi_1'' - \frac{1^2 \cdot 3 \cdot 5}{2^2 \cdot 4^2}\frac{1}{\mu^4}\cdot\phi_2'' + \frac{1^2 \cdot 3^2 \cdot 5 \cdot 7}{2^2 \cdot 4^2 \cdot 6^2}\frac{1}{\mu^6}\phi_6'' + \ldots (E)$$

in which

$$\phi_0'' = \log 4\mu - 2$$

$$\phi_1'' - \phi_0'' = \frac{1}{1} - \frac{1}{3} + \frac{1}{1}$$

$$\phi_2'' - \phi_1'' = \frac{1}{2} - \frac{1}{5} - \frac{1}{1}$$

$$\phi_3'' - \phi_2'' = \frac{1}{3} - \frac{1}{7} - \frac{1}{3}$$

$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad .$$

$$\phi_n'' - \phi_{n-1}'' = \frac{1}{n} - \frac{1}{2n+1} - \frac{1}{2n-3}$$

(C) and (D) are valid for all distances of the circles, but converge most rapidly when the circles are close together.

(E) converges only if $k^2 > \frac{1}{2}$. The first five terms of this formula have been given by Rosa (*loc. cit.* p. 16).

5. *Self-induction of a Solenoid.*

Take the diameter of the solenoid as unit of length, let the axial length of the solenoid be z, and the number of turns be nz. Then, if M represents the mutual induction between two equal coaxial circles at distance z, the mutual induction between the solenoid and an equal circle in the plane of its end

is $\quad n \displaystyle\int_0^z M\, dz,$ and the self-induction required is

$$2n^2 \int_0^z dz \int_0^z M\, dz.$$

Now from (3 d), since $y_4 = M$, $x_4 = -z^2$,

$$\frac{d}{dz}\left\{ (z + z^3)\frac{dM}{dz} \right\} = 3zM,$$

so that by integration

$$(z + z^3)\frac{dM}{dz} = 3z\int M\, dz - 3\int dz \int M\, dz,$$

$$(z + z^3)M = (1 + 3z^2)\int M\, dz - 3z\int dz \int M\, dz,$$

from which

$$\int \mathrm{M}\,dz = (z+z^3)\left(\mathrm{M}-z\frac{d\mathrm{M}}{dz}\right),$$

$$\int dz \int \mathrm{M}\,dz = \tfrac{1}{3}(z+z^3)\left\{3z\mathrm{M}-(1+3z^2)\frac{d\mathrm{M}}{dz}\right\} \qquad (7)$$

Using the value of M given by (1), and remembering that $k^2 = \dfrac{1}{1+z^2}$, we obtain from (7)

$$\int \mathrm{M}\,dz = 2\pi\frac{k'}{k^2}(\mathrm{K}-\mathrm{E}),$$

$$\int dz \int \mathrm{M}\,dz = \frac{2\pi}{3k^3}\{(1-k^2)\mathrm{K}-(1-2k^2)\mathrm{E}\}.$$

Hence the self-induction sought is

$$\mathrm{L} = 2n^2\int_0^z dz \ \overset{z}{\underset{0}{}}\mathrm{M}\,dz,$$

$$= \frac{4\pi n^2}{3k^3}\{(1-k^2)\mathrm{K}-(1-2\,k^2)\mathrm{E}-k^3\}.$$

This holds when the diameter is unity. If the diameter is $2a$ and the length b, put $z=b/2a$, so that $k^2 = \dfrac{4a^2}{4a^2+b^2}$, and (by dimensions) multiply by $(2a)^3$. Then

$$\mathrm{L} = \frac{32}{3}\frac{\pi n^2 a^3}{k^3}\{(1-k^2)\mathrm{K}-(1-2k^2)\mathrm{E}-k^3\}. \qquad (8)$$

This expression was first given by Lorenz [*]. Proofs have also been supplied by Coffin [†] and by Russell [‡]. The author believes the above proof to be new.

6. By treating equation (8) in the same way as (1) was treated, various series can be obtained for L.

Thus,

$$\mathrm{L} + \frac{32}{3}\pi n^2 a^3$$

satisfies the equation

$$k^2(1-k^2)\frac{d^2y}{dk^2} + 5k(1-k^2)\frac{dy}{dk} + 3y = 0,$$

* Wied. *Ann.* vii. p. 161 (1879).
† Bull. Bureau of Standards, ii. p. 123 (1906).
‡ Phil. Mag. xiii. p. 445 (1907).

or putting

$$k^2 = x, \quad \vartheta = x\frac{d}{dx}, \quad u = x^{\frac{1}{2}}y,$$

$$\vartheta(\vartheta+1)u = x\left(\vartheta+\frac{3}{2}\right)\left(\vartheta-\frac{1}{2}\right)u, \quad . \quad . \quad . \quad (9)$$

an equation of the type (4).

The solutions of (9) with the various possible independent variables yield the following series :—

$$L = \frac{8\pi^2 n^2 a^3}{k}\left\{ F\left(\frac{3}{2}, -\frac{1}{2}, 2, k^2\right) - \frac{4}{3\pi}k \right\}, \quad . \quad . \quad . \quad (F)$$

$$= \frac{8\pi^2 n^2 a^3}{k}\left\{ (1-k^2)F\left(\frac{5}{2}, \frac{1}{2}, 2, k^2\right) - \frac{4}{3\pi}k \right\}, \quad . \quad . \quad (G)$$

$$= 4\pi^2 n^2 a^2 b\left\{ F\left(\frac{1}{2}, -\frac{1}{2}, 2, -\frac{4a^2}{b^2}\right) - \frac{8}{3\pi}\frac{a}{b} \right\}, \quad . \quad . \quad (H)$$

$$= 4\pi^2 n^2 a^2 b\left\{ \left(\frac{4a^2+b^2}{b^2}\right)^2 F\left(\frac{3}{2}, \frac{5}{2}, 2, -\frac{4a^2}{b^2}\right) - \frac{8}{3\pi}\frac{a}{b} \right\}, \quad (I)$$

in which $F(\alpha, \beta, \gamma, x)$ denotes the hypergeometric series

$$1 + \frac{\alpha\beta}{1\cdot\gamma}x + \frac{\alpha(\alpha+1)\beta(\beta+1)}{1\cdot 2\cdot\gamma(\gamma+1)}x^2 + \ldots.$$

The above series are suitable for long coils. (F) and (G) are convergent for all lengths. (H) and (I) converge only if $b > 2a$.

$$L = \frac{16\pi n^2 a^3}{k}\left\{ \frac{2}{3}(1-k) + k'^2\psi_1 + \frac{1\cdot 5}{2\cdot 4}k'^4\psi_2 \right.$$
$$\left. + \frac{1\cdot 3\cdot 5\cdot 7}{2\cdot 4\cdot 4\cdot 6}k'^6\psi_3 + \frac{1\cdot 3\cdot 5\cdot 5\cdot 7\cdot 9}{2\cdot 4\cdot 6\cdot 4\cdot 6\cdot 8}k'^8\psi_4 + \ldots \right\}, \quad . \quad (J)$$

in which

$$\psi_1 = \log\frac{4}{k'} - \frac{5}{6}$$

$$\psi_2 - \psi_1 = \frac{1}{2} + \frac{1}{4} - \frac{1}{1} - \frac{1}{5}$$

$$\psi_3 - \psi_2 = \frac{1}{4} + \frac{1}{6} - \frac{1}{3} - \frac{1}{7}$$

$$\psi_4 - \psi_3 = \frac{1}{6} + \frac{1}{8} - \frac{1}{5} - \frac{1}{9}$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$L = \frac{16\pi n^2 a^3}{k^3} \left\{ \frac{2}{3}(1-k^3) + k'^2\psi_1' - \frac{1.3}{2.4}k'^4\psi_2' \right.$$
$$\left. - \frac{1.1.3.5}{2.4.4.6}k'^6\psi_3' - \frac{1.1.3.3.5.7}{2.4.6.4.6.8}k'^8\psi_4' - \ldots \right\}, \quad (K)$$

in which

$$\psi_1' = \log\frac{4}{k'} - \frac{3}{2}$$
$$\psi_2' - \psi_1' = \frac{1}{2} + \frac{1}{4} + \frac{1}{1} - \frac{1}{3}$$
$$\psi_3' - \psi_2' = \frac{1}{4} + \frac{1}{6} - \frac{1}{1} - \frac{1}{5}$$
$$\psi_4' - \psi_3' = \frac{1}{6} + \frac{1}{8} - \frac{1}{3} - \frac{1}{4}$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$L = 16\pi n^2 a^3 \left\{ \left(\frac{b}{2a}\right)^2\psi_1'' + \frac{1.1}{2.4}\left(\frac{b}{2a}\right)^4\psi_2'' - \frac{1.1.1.3}{2.4.4.6}\left(\frac{b}{2a}\right)^6\psi_3'' \right.$$
$$\left. + \frac{1.1.3.1.3.5}{2.4.6.4.6.8}\psi_4'' - \ldots\ldots\ldots \right\}, \quad \ldots \quad (L)$$

in which

$$\psi_1'' = \log\frac{8a}{b} - \frac{1}{2}$$
$$\psi_2'' - \psi_1'' = \frac{1}{2} + \frac{1}{4} + \frac{1}{1} - \frac{1}{1}$$
$$\psi_3'' - \psi_2'' = \frac{1}{4} + \frac{1}{6} - \frac{1}{1} - \frac{1}{3}$$
$$\psi_4'' - \psi_3'' = \frac{1}{6} + \frac{1}{8} - \frac{1}{3} - \frac{1}{5}$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$L = \frac{16\pi n^2 a^3}{k^4} \left\{ \frac{2}{3}(1-k^4) + \left(\frac{b}{2a}\right)^2\psi_1''' - \frac{3.5}{2.4}\left(\frac{b}{2a}\right)^4\psi_2''' \right.$$
$$\left. + \frac{3.5.5.7}{2.4.4.6}\left(\frac{b}{2a}\right)^6\psi_3''' - \frac{3.5.7.5.7.9}{2.4.6.4.6.8}\left(\frac{b}{2a}\right)^8\psi_4''' + \ldots \right\}, \quad (M)$$

in which

$$\psi_1''' = \log \frac{8a}{b} - \frac{11}{6}$$

$$\psi_2''' - \psi_1''' = \frac{1}{2} + \frac{1}{4} - \frac{1}{3} - \frac{1}{5}$$

$$\psi_3''' - \psi_2''' = \frac{1}{4} + \frac{1}{6} - \frac{1}{5} - \frac{1}{7}$$

$$\psi_4''' - \psi_3''' = \frac{1}{6} + \frac{1}{8} - \frac{1}{7} - \frac{1}{9}$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

The above series are suitable for short coils. (J) and (K) are convergent for all lengths. (L) and (M) converge only if $b < 2a$.

XXXV. *On an Optical Test for Angles of Contact.*
By Prof. A. ANDERSON, *M.A., and* J. E. BOWEN, *M.A.*[*]
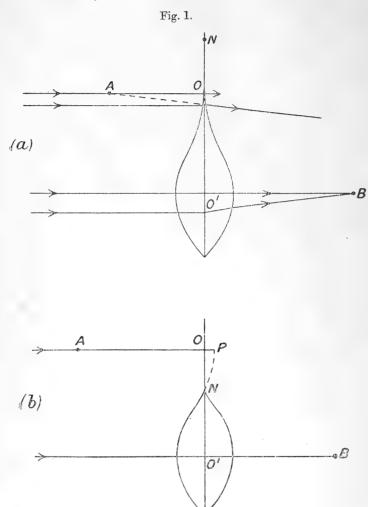
IN the February Number of the ' Philosophical Magazine ' we gave a method of determining surface-tensions from observations on the heights to which liquids rise in tubes, which is free from corrections of any kind, and the accuracy of which depends entirely on the capabilities of a measuring microscope. We showed how, by plotting curves giving the relation between the radius of the tube and the radius of curvature at the centre of the meniscus, the angle of contact could be deduced. The curves obtained for water and some other liquids showed that—at least, very approximately—this angle was zero.

The following experiment was designed to test directly whether any angle of contact differing from zero really exists in the case of water and some other liquids which were examined. If a rectangular piece of very thin glass be dipped in a liquid and then held in a vertical plane with two of its edges horizontal, there will be a long cylindrical drop attached to it. Its cross-section or the appearance it presents when looked at endwise is one of the forms represented in the figure (fig. 1).

Fig. 1 (*a*) is drawn on the supposition that the angle of contact is zero. It will be seen that the drop forms two cylindrical lenses, one convex with centre at the point O', the other (only the lower half of which is present) being

Fig. 1.

concave with centre at O, the point where the glass plate is tangential to the contour of the drop. The upper edge of the drop may be along the line through O perpendicular to the plane of the paper, or may be higher up at some point N. If a

collimator with its axis horizontal and with a horizontal slit be placed to the left of the drop, parallel light will fall perpendicular to the glass plate as shown in the figure, and the concave lens will form an image of the slit, which will be a straight line through O perpendicular to the plane of the paper, and in the same horizontal plane as the corresponding line through O. If now a low-power microscope be placed to the right of the drop with its axis along OA, the image of the slit formed at A can be seen and arranged to coincide with the horizontal cross-wire of the microscope. If the microscope be now moved back through a distance AO it will be focussed on the glass plate, and the image in the microscope of the upper edge of the drop should either coincide with the horizontal cross-wire of the microscope or it should be necessary to raise the microscope vertically to make it do so.

If an angle of contact existed, the drop would present the appearance of fig. 1 (*b*). The continuation of one side of the drop has been dotted in to the point P, where it would become vertical ; and it will be observed that in this case the centre of the lens O which is in the same horizontal plane as P is above the upper edge of the drop. Thus after focussing the microscope on A, getting the image to coincide with the horizontal cross-wire, and then moving it back through the distance AO so as to focus on the glass plate, the microscope must be lowered a distance ON to get the image of the upper edge of the drop to coincide with the cross-wire.

The microscope used was the Bailey & Smith microscope used in the previous experiment (*loc. cit.*). This was capable of horizontal and vertical motions, and was arranged with axis along the line of parallel light and its horizontal motion along this line. A clean microscope slide-cover was used as the glass plate and the liquids examined were those of the former experiment—water, glycerine, olive-oil, and turpentine. In all of these when the drop was freshly formed a perfectly straight image of the slit was seen, and to get the image of the upper edge of the drop (sometimes marked by a line of extremely minute air-bubbles) to coincide with the cross-wire when the microscope was brought back the microscope had to be raised. The image of this edge was not straight. As evaporation went on the upper edge came down to the same level as A (which of course also moved, both vertically and in a horizontal direction perpendicular to the plate); and as evaporation proceeded further the image became curved and took the shape of the upper edge of the drop. No indication of the state of things represented in fig. 1 (*b*) could be

observed.   Hence it was concluded that the angles of contact in the cases examined were zero.

As the liquid on the two sides does not evaporate at quite the same rate, the upper edges on the two sides do not always coincide : thus a better examination can be made if only one side of the plate be wet and only half the drop shown in the figure be formed.

If the argument used above is correct, it is possible to use the experiment as a rough method of measuring surface-tensions.   To do this we consider the convex lens also, which has its centre at O′, and which brings the parallel light to a focus at B.

Let a = OA.

b = O′B.

h = vertical distance between OA and O′B.

r_1 = radius of curvature of each face of concave lens (assuming curvature the same).

r_2 = radius of curvature of face of convex lens.

μ = refractive index of liquid.

ρ = density of liquid.

p_1 = pressure inside liquid at O.

p_2 =   ,,   ,,   ,,   O′.

π = atmospheric pressure.

T = surface-tension of liquid.

Treating the lens as thin,

$$\frac{1}{a} = (\mu - 1)\frac{2}{r_1}, \qquad \frac{1}{b} = (\mu - 1)\frac{2}{r_2},$$

$$p_2 = \pi + \frac{T}{r_1},$$

$$p_1 = \pi - \frac{T}{r_2} ;$$

$$\therefore \quad p_2 - p_1 = T\left(\frac{1}{r_1} + \frac{1}{r_2}\right) = \frac{T}{2(\mu - 1)}\left(\frac{1}{a} + \frac{1}{b}\right).$$

But $p_2 - p_1 = g\rho h$;

$$\therefore \quad T = 2g\rho(\mu - 1)hab/(a + b).$$

If only one side of the plate is wet with the liquid, the formula becomes

$$T = g\rho(\mu - 1)hab/(a + b).$$

As the microscope was fitted with verniers for both horizontal and vertical movements, the readings were easily taken. The method is, of course, not capable of great accuracy, owing to the changes taking place in the drop due to evaporation. In the case of a liquid which evaporates quickly (*e. g.* turpentine) the readings must be taken very rapidly.

The following are some measurements taken in this way, which appear to be sufficiently close to show that the argument is correct :—

Water.

$a = \cdot 644$	$b = \cdot 544$	$h = \cdot 392$	$T = 75 \cdot 6$
$\cdot 764$	$\cdot 673$	$\cdot 350$	$78 \cdot 2$
$\cdot 932$	$\cdot 66$	$\cdot 294$	$73 \cdot 5$

Turpentine.

$a = \cdot 674$	$b = \cdot 331$	$h = \cdot 151$	$T = 26 \cdot 9$
$\cdot 576$	$\cdot 396$	$\cdot 15$	$28 \cdot 2$
$\cdot 661$	$\cdot 354$	$\cdot 148$	$27 \cdot 4$

Glycerine.

$a = \cdot 443$	$b = \cdot 287$	$h = \cdot 370$	$T = 74 \cdot 9$
$\cdot 435$	$\cdot 344$	$\cdot 337$	$75 \cdot 2$
$\cdot 358$	$\cdot 400$	$\cdot 344$	$75 \cdot 5$
$\cdot 367$	$\cdot 338$	$\cdot 392$	$74 \cdot 4$
$\cdot 308$	$\cdot 369$	$\cdot 382$	$74 \cdot 5$

a, b, h are in cm., T in dynes per cm. It will be noticed that though the method gives values for water and turpentine in the neighbourhood of those generally accepted, the values for glycerine, though consistent with each other, are too high. This may be due to the fact that the glycerine drop is much thicker than either of the others, and the formula for thin lenses may not apply; or it may be due to the rapid absorption of aqueous vapour from the air.

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XXXVI. *The Theory of the Flicker Photometer.*—II. *Unsymmetrical Conditions.* *By* HERBERT E. IVES *and* E. F. KINGSBURY [*].

SYNOPSIS.

1. Introduction.
2. The Sensibility of the Flicker Photometer.
3. Critical Frequency-Illumination Relations with Superposed Steady and Flickering Illuminations.
4. Critical Frequency-Illumination Relations with Unequal Light and Dark Intervals.
      (*a*) Theoretical.
      (*b*) Experimental.
      (*c*) Discussion.
5. The Flicker Photometer with Unequal Exposures of the Compared Colours.
6. Some Effects of Accidental Dissymmetry on the Critical Frequency and Flicker Photometer Phenomena.
7. Summary.

1. *Introduction.*

IN a previous paper † we have developed a theory of the action of the flicker photometer. The essential part of that theory consists in the treatment of the visual apparatus as a conducting layer of matter receiving and transmitting intermittent radiation according to the general physical laws of conduction. The principal assumptions are as follows :—

1. That the stimulus is transmitted by a medium having a certain "diffusivity," by reason of which the amplitude of a fluctuating stimulus is reduced.

2. That the disappearance of flicker occurs when the *ratio* of maximum to minimum of the transmitted impression has a certain value.

By the application of the Fourier conduction equation, on the basis of these assumptions, it was shown that the behaviour of the flicker photometer toward different colours and at different intensities may be derived from the behaviour of the colours separately with respect to the critical speed of disappearance of flicker.

The previous paper dealt only with what may be termed symmetrical conditions. Critical frequency relations were studied only for equal dark and light exposures, the flicker photometer was considered only for that case where the two

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* Communicated by the Authors.
† "The Theory of the Flicker Photometer," Ives & Kingsbury, Phil. Mag. Nov. 1914, p. 708.

compared colours are exposed for equal times, and the only setting of the flicker photometer which was the subject of numerical study was the equality point.

In the present paper a study is made, on the basis of the same assumptions, of certain unsymmetrical conditions. These conditions are much more difficult to treat. They necessitate, for instance, definite knowledge of the value, under various unusual conditions, of the Fechner fraction, and of the relative effect of impressions of different waveform on the ultimate receiving apparatus. Their complete treatment is in some cases practically impossible without certain simplifying assumptions, which are not in entire accord with known facts.

Partly—perhaps, principally—on this account the further development of the theory presented here is not entirely satisfactory. But, while it fails to fit the experimental facts quantitatively as closely as we would hope, it does handle the principal phenomena qualitatively in a very striking manner, and, moreover, has prompted experimental work whose results must receive consideration in the development of any theory of flicker photometry.

2. *The Sensibility of the Flicker Photometer.*

Of the two methods of utilizing flicker for the measurement of light, one—the frequency of disappearance of flicker—is quite insensitive, the other—the point at which two alternated illuminations show a minimum of flicker—is quite sensitive. It is for this reason that the flicker photometer proper is deserving of consideration as an instrument of precision, while the critical frequency phenomena are of little value in measurement.

The low sensitiveness of the critical frequency method is, as far as the mode of treatment here followed goes, simply a matter of experimental fact. The error of setting for critical speed amounts to one or two cycles per second, which means for ordinary intensities 25 to 50 per cent. in illumination. Add to this the fact that variations in conditions of adaptation, &c., cause uncertainties fully as large, and the unsatisfactory character of the method for measurement is clear.

How, then, can the flicker photometer, whose behaviour we have endeavoured to predict from the critical frequency phenomena, possess the sensibility it does? This greater sensibility we find is shown by the straightforward application of the theory as presented in the former paper, as follows :—

Let us consider the case of no colour difference. At the condition of equality, with an ideal flicker photometer, no flicker results, no matter what the speed of alternation. The critical speed is therefore zero. As the equality point is deviated from in either direction a flickering condition is produced due to the alternation of the two unequal illuminations. The speed necessary to make this flicker disappear may be determined by the ordinary experimental method for various known differences of illumination. When sufficient points have thus been fixed, the lines joining them enclose a space within which no flicker occurs. At any given speed the limits of the no-flicker space indicate the limits within which the flicker photometer setting must lie. The sensibility of the flicker photometer may thus be indicated graphically by the narrowness of this region.

Let I_1 be the illumination of one side of the flicker photo-
meter.

I_2 that of the other side. (We shall in this paper distinguish between the actual illumination and the apparent illumination, which latter refers to the appearance of the disk when running, and is always $I \times$ angular opening. This usage causes the difference of the constants in certain of the equations common to the two papers.)

Let us, as in the previous paper, deal with stimuli represented by simple sine curves. Then, as before, the ranges of the two transmitted impressions at a depth X are

$$\left. \begin{array}{ll} I_1 e^{-X\sqrt{\frac{\omega}{2K}}}, & K = \text{diffusivity} \\[2mm] I_2 e^{-X\sqrt{\frac{\omega}{2K}}}, & \omega = \text{speed} \end{array} \right\} \quad . \quad . \quad (1)$$

The total resultant range is the difference between these or

$$e^{-X\sqrt{\frac{\omega}{2K}}}[I_1 - I_2]. \quad . \quad . \quad . \quad . \quad . \quad (2)$$
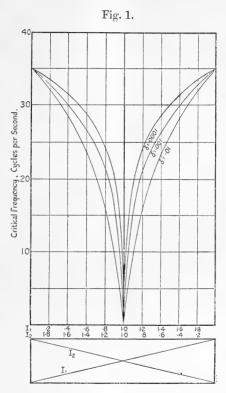
The fractional part this is of the whole, or the fractional range is

$$2e^{-X\sqrt{\frac{\omega}{2K}}}\left[\frac{I_1 - I_2}{I_1 + I_2}\right]. \quad . \quad . \quad . \quad . \quad (3)$$

Calling this fractional range a constant, δ, according to our previous assumption, and solving for ω, we obtain

$$\omega = \frac{2\left[\log\frac{2}{\delta} + \log\frac{I_1 - I_2}{I_1 + I_2}\right]^2}{\frac{X^2}{K}[\log e]^2}. \quad . \quad . \quad . \quad (4)$$

In fig. 1 are shown calculated values of ω, for the simplest possible photometric condition, namely that where the total illumination is maintained constant. This means that we are here free from any questions as to the rate of change of diffusivity or of the Fechner fraction with the illumination.

Fig. 1.

The sensibility characteristics of the Flicker Photometer as exhibited by the critical frequency of disappearance of flicker for various ratios of the two compared lights. Calculated curves for the case of total illumination maintained constant. Various values of the Fechner fraction (δ).

Curves are shown for three values of δ, namely, $\cdot01$, $\cdot001$, and $\cdot0001$. An experimental value for ω has been taken for the limiting conditions, and the value used for the diffusivity solved for from the equation (4).

The figure shows with what extraordinary rapidity the critical speed rises as the two illuminations become unequal. Thus a variation of only about one per cent. causes as great a change in the critical frequency as did fifty per cent. in

the ordinary critical frequency relation. The sensibility of
the flicker photometer is measured by the width of the
no-flicker region, as already noted. This is extremely small
—a matter of a few per cent.—for low speeds, even for the
largest value of δ. The figure clearly shows the desirability
of using as low a speed as possible, which means the careful
elimination of all mechanical flicker. It is obvious why the
sensibility of the flicker photometer decreases with increasing
colour difference, since this necessitates a higher speed and
consequent wider zone of possible setting.

The case just considered was not studied by us experi-
mentally, as our arrangement of apparatus did not make
this convenient. We have, however, obtained data for the
common case where one illumination is maintained constant
while the other varies. The calculation of this case is like
that of the preceding, except that it becomes necessary to
introduce a changing value of the diffusivity (and possibly
of the Fechner fraction) as the mean illumination changes.
In accordance with the results of the previous paper we have
assumed the diffusivity to vary according to the relation

$$k = X^2(a \log I_A + b), \quad \ldots \quad \ldots \quad (5)$$
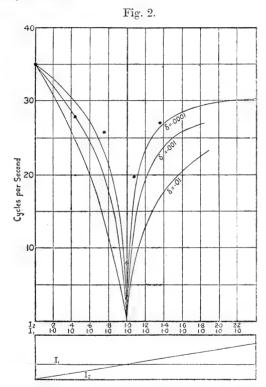
where I_A is the *average* value of the illumination, the con-
stants being derived from experimental critical frequency
relations and the formulæ previously developed.

Fig. 2 shows the calculated curves for various values of δ,
and a set of experimental points. (The apparatus used is
described under a later section.)

It is to be noted, first of all, that both theoretical and
experimental curves show a lack of symmetry, the median
lying for low speeds toward the fixed light, at high speeds
toward the movable one. This is a point of very great
practical importance. The obvious moral is that the photo-
metric arrangement should be such that the mean illu-
mination remains constant, that is, as the illumination on
one side is increased that on the other should be decreased,
as was done in the first case considered and shown in fig. 1.
The effect of this lack of symmetry is, at the speeds which
would ordinarily be used, to displace the setting toward the
fixed illumination, which is therefore under-rated. In most
practical cases, with a good design of flicker photometer, the
effect of this lack of symmetry would be largely eliminated
where a strict substitution method is employed. If, however,
colours are measured which call for greatly different speeds,
the displacement will be different for each. This difference
could amount to as much as two per cent., judging from

speed-data recorded in an earlier paper [*], for red and green light, using the experimental values of fig. 2. This is, therefore, a point which should receive careful attention in the future design of apparatus to be used in large colour-difference work, such as the determination of spectral luminosity curves.

Fig. 2.

Sensibility characteristics of the flicker photometer. Calculated curves for various values of δ for the case where one illumination is constant, the other variable. Experimental values are shown by dots.

The second point to be noted is that the experimental values agree most nearly with those calculated from a very small value of the Fechner fraction, namely ·0001. The actual value of this fraction for simultaneously presented juxtaposed surfaces is between ·0025 and ·01. Why is this small value apparently called for?

* "Spectral Luminosity Curves obtained by the Equality of Brightness Photometer and the Flicker Photometer under Similar Conditions," Ives, Phil. Mag. July 1912, p. 149.

This point illustrates the remark made in the introduction, that the cases to be treated in this paper demand definite numerical values which are not in all cases known, and call for simplifying assumptions which are not completely justified. We may state in regard to this quantitative discrepancy between the calculated and observed facts that:

1. We do not actually know what the value of the Fechner fraction is for successively presented impressions; it may be much lower than for the cases so far studied experimentally.

2. Our theoretical treatment is for a simple sine curve stimulus, while the experimental work was done with disks having an abrupt dividing edge.

3. Any unevenness of the surface of disks such as we used will tend greatly to increase the speed called for at all points except at what is the left-hand end of the diagram shown. This point will be treated in detail under another section.

Whether these considerations are entirely sufficient to account for the apparent exaggeration of the experimental over the calculated conditions we are unable to determine. However, it is evident that the theory does account extraordinarily well for the principal facts regarding the sensibility of the flicker photometer.

Before leaving the question of sensibility we may call attention to an apparent consequence of the theory of some practical importance. It has to do with the character of the transition from one stimulus to the other. Should this be abrupt or gradual? Referring to fig. 1, it is to be noted that if the transition, which is there considered as gradual, is made abrupt, the limiting critical speeds, where either light is reduced to zero value, will, for fairly obvious reasons, be increased. Since the lower limit of speed is fixed (zero), this means that the no-flicker region will be narrower with the abrupt transition. In short, the sensibility *for a given speed* should be greater for an abrupt transition than for a gradual; for instance, it should be greater for a sharp transition flicker-photometer field in focus than for the same field out of focus. We are informed that some recent experimental work confirms this. Where, however, the speed is adjusted to the minimum set by the disappearance of colour flicker, it is probable that the minimum will be so much lower with the gradual transition as to leave the ultimately attained sensibility about the same with either type of transition.

3. *Critical Frequency-Illumination Relations with Super-posed Steady and Flickering Illuminations.*

Before leaving the equations developed to indicate the sensibility of the flicker photometer, it is of interest to note that they show as well the behaviour, on our theory, of a flickering illumination superposed on a steady one. Thus equation (4), while developed to represent the case of two dovetailed flickering illuminations of unequal intensity, represents as well the case of a steady illumination, of the value of the lesser illumination, upon which is superposed a fluctuating illumination of the amplitude of the difference of the two illuminations.

What will be the behaviour of a fluctuating illumination of this character as the illumination is varied? So far as the authors are aware this case has not been studied experimentally. We obtain an answer by combining equations (4) and (5), which give

$$\omega = \frac{2\left[\log\frac{2}{\delta} + \log\frac{I_1 - I_2}{I_1 + I_2}\right]^2}{[\log e]^2}[a\log I_\Lambda + b]. \quad . \quad . \quad (6)$$

The most striking characteristic of this expression is evident upon inspection, namely that each different ratio of steady to flickering light calls for a different *slope* (coefficient of $\log I_\Lambda$) in the critical frequency-log I plot.

We may calculate the critical frequency-log I lines as follows :—
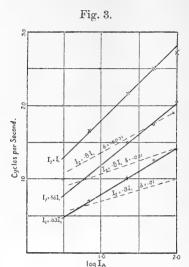
Let experimental values of ω be taken at two illuminations for the ordinary experimental case of $I_2 = 0$. Assume a value for δ. From this a and b may be obtained, which constitute all the data necessary.

In fig. 3 are shown, first, an experimental critical frequency-log I line, for the case of $I_2 = 0$, obtained with an abrupt transition disk, then the corresponding line as calculated for a ratio of $\frac{I_2}{I_1}$ of ·8, for three values of δ. Finally are shown lines obtained by experiment for ratios of $\frac{I_2}{I_1}$ of ·83 and ·56. It will be noted that in their most novel characteristic—the variation of slope—the experimental lines verify the prophesy of theory.

As in the matter of sensibility, the correspondence between theory and experiment is not quantitatively all that could

be desired. The best correspondence would call for a value of δ of about ·001, but even with this small value the slope of the theoretical line is too great. We would again point out that while the theoretical work is done for the case of

Fig. 3.

Phenomena of superposed steady and flickering illuminations. Dashed lines calculated from theory. Full lines, experimental values, showing varying inclinations as suggested by theory, but actual slope and magnitudes not as calculated from simplest assumptions.

gradual transitions, the experimental is done with abrupt transitions. In addition, our assumption that the diffusivity varies with the logarithm of the mean illumination may be wrong. It is, for instance, possible that the diffusivity is a function of an illumination intermediate between the maximum and the mean. Mechanical defects of the photometric field may as well be active as disturbing causes.

These points are, however, secondary to the fact that the theory accounts for and, in fact, has prophesied the predominating characteristics of the cases considered. In both it is evident that information of some value would be furnished by performing the experimental work with apparatus giving the exact kind of transition which is treated by the theory. The experimental difficulties of obtaining a sine-curve transition from one illumination to another are, however, rather formidable, and we have not felt the slight additional support which might be furnished to the theory to warrant undertaking the great additional labour.

4. *Critical Frequency-Illumination Relations with Unequal Light and Dark Intervals.*

(a) *Theoretical.*

Our theory of the flicker photometer is essentially a theory of the action of the eye toward intermittent excitation by light. The action of the flicker photometer follows on this theory directly from the critical-frequency-illumination laws. In undertaking an examination of the flicker photometer for the case where the two lights are exposed for unequal intervals—one of the principal objects of the study—it is therefore necessary to test the sufficiency of our theory to explain the critical frequency relations for unequal light and dark intervals.

The most extensive study of this case is that of T. C. Porter[*]. He experimented with a series of disks, part white, part black, and obtained results which he found well represented by the equation

$$n = a + (b + c \log I) \log w (360 - w), \quad . \quad . \quad (7)$$

where w is the size of the white sector in degrees, n = cycles per second, I = illumination, a, b, and c constants.

This equation, which has no theoretical basis, indicates that the critical frequency should be a maximum for $w = 180$ degrees; that the curves connecting critical frequency with angle should be symmetrical about 180 degrees; that the $\log I$ critical frequency straight lines should have a different inclination for each angle of opening (except complementary angles, which have the same). His actual numerical values call for a large *negative* frequency at 0 and 360 degrees, instead of zero, and the equation is not satisfactory for small angles at illuminations below the change in slope of the straight critical speed-log I lines.

While it is not necessary that our theory should yield the same formula as that developed by Porter, we must be able to explain the dominating phenomenon, namely the reduction of speed as the white opening is either increased or decreased from 180 degrees.

Let us consider two complementary disks, of white angles less than and greater than 180 degrees respectively. Let these be rotated at some finite speed. Suppose the diffusivity of the receiving and transmitting medium of the eye to be the same as either disk is observed. It is obvious that (under this restricting condition) the two damped fluctuating impressions which are transmitted to any given depth must

[*] "Studies in Flicker," Porter. Proc. Roy. Soc. vol. lxiii. p. 347 ; vol. lxx. p. 313 ; vol. lxxxvi. p. 445.

be exactly complementary ; in other words, their range of fluctuation of value must be equal. But while the actual range is alike, the fractional range, in terms of the mean value, which on our theory determines the disappearance of flicker, will be small for the large white opening, and large for the small white opening. It is easy to see that (the diffusivity being fixed) the critical speed must increase progressively from zero to 360 degrees white opening to large values for small openings. But, according to our theory, the diffusivity varies with the illumination and in the same direction. It is to be expected that it is the average illumination (or, strictly speaking, the average brightness), the product of illumination and white opening, that determines the diffusivity. Accordingly we may expect the diffusivity to decrease from a maximum at 360 degrees to very low values for small angles. Lowered diffusivity calls for lower speed of alternation to produce the same range. We therefore have, according to our theory, two opposing effects : one, which we may call a contour effect, calling for increasing speed as the white angle decreases ; the other, the diffusivity effect, which calls for decreasing speed as the white opening becomes small. If our theory is correct, the resultant of of the two should have a maximum at $180°$. The adequacy of these effects to explain the experimental facts can, of course, be determined only by quantitative calculations, which we shall now attempt.

Here we cannot, as in the case formerly treated, assume a simple sine curve stimulus. We have therefore approached the problem in a different manner. We have first developed the complete Fourier series expansion for unequal light and dark intervals, with abrupt transitions, as follows :

$$I_s = I\phi + \frac{2I}{\pi}\left[\sin \pi\phi \cos \omega t + \frac{1}{2}\sin 2\pi\phi \cos 2\omega t \right.$$
$$\left. + \frac{1}{3}\sin 3\pi\phi \cos 3\omega t + ...\right]. \quad (8)$$

We have then combined this, in the same manner as in our earlier paper, with the fundamental Fourier conduction equation.

The result is the following infinite series:

$$I_s = I\phi + \frac{2I}{\pi}\left[e^{-X\sqrt{\frac{\omega}{2K}}}\sin \pi\phi \cos\left(\omega t - X\sqrt{\frac{\omega}{2K}}\right) \right.$$
$$\left. + \frac{1}{2}e^{-X\sqrt{\frac{\omega}{K}}}\sin 2\pi\phi \cos\left(2\omega t - X\sqrt{\frac{\omega}{K}}\right) + ...\right], \quad (9)$$

where

    I_s = transmitted impression.
    I = intensity of stimulus.
    ϕ = fraction of cycle during which stimulus is acting.
    t = time.
    ω = frequency.
    X = distance from surface of medium.
    K = diffusivity.

Were we in possession of extensive tables of values of this expression for a wide range of values of ϕ, X, ω, and K, it would be possible to pick out those values of ω which, for any chosen combination of the other variables, would make the fractional range of fluctuation whatever we chose. Such tables are not, however, available, and this is a problem in heat conduction which has not apparently been investigated experimentally. No simple method of solving for the range of fluctuation or for ω has been found by us, and, as a consequence, we have had to be content with a rough and approximate solution.

In default of the complete solution we have worked with the simplified expression furnished by the first two terms only.

The range is given by the difference between the maximum and minimum values of the cosine term, or

$$R = \frac{4}{\pi} I e^{-X\sqrt{\frac{\omega}{2K}}} \sin \pi\phi, \quad . \quad . \quad . \quad (10)$$

the fractional range is this divided by the mean value, and this we assume, for the condition of no flicker, to be a certain small quantity which we have called δ, or

$$\delta = \frac{4}{\pi\phi} e^{-X\sqrt{\frac{\omega}{2K}}} \sin \pi\phi. \quad . \quad . \quad . \quad (11)$$

Taking logarithms,

$$\omega = 2 \left[\frac{\log \frac{4}{\pi} + \log \sin \pi\phi - \log \phi - \log \delta}{\log e} \right]^2 \frac{K}{X^2}. \quad . \quad (12)$$
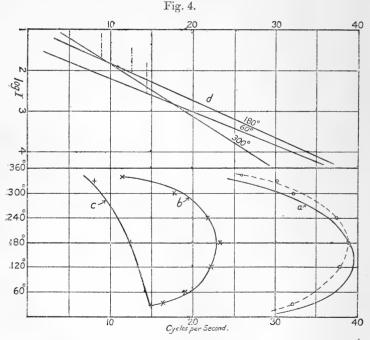
If, now, for the diffusivity we introduce the value derived in the former paper (equation (7) of that paper), substituting the mean illumination for the illumination there used, and also using the actual values of the constants, in place of the

symbols (m and p) there used, we finally obtain for the complete expression,

$$\omega = \left(\frac{\log \frac{4}{\pi} + \log \sin \pi\phi - \log \phi - \log \delta}{\log 2 - \log \delta} \right)^2 (a \log \mathrm{I}\phi + b), \quad (13)$$

where a and b are the experimentally found constants for a 180-degree disk under an illumination I. (The quantity outside the brackets should, of course, reduce to unity for the case of 180 degrees opening. The outstanding error is one of the consequences of using the approximate two-term expression. The term $\log \frac{4}{\pi}$ has been dropped in most of the calculations below.)

In fig. 4 are plotted curves showing the values of ω as

Fig. 4.

Lower diagram.—Full lines, calculated critical frequencies for different angular openings. a, high illumination; b, medium illumination; c, low illumination for blue light. Circles and crosses give experimental values.

Upper diagram.—Calculated critical frequency-log I lines for three angular openings. Dotted lines indicate characteristics for blue light at low intensities. All calculated data are on a basis of $\delta = \cdot 001$.

given by this equation under various conditions of illumination. These are all worked out for a value of δ of ·001.

Curves *a* and *b* show the speeds called for at two illuminations for white sectors from zero to 360 degrees. It will be seen that the maximum near 180 degrees, and the drop toward zero for both large and small angles, are predicted, in general agreement with the findings of Porter. Unlike the curves given by Porter's equation these are somewhat unsymmetrical.

Curve *c* shows a very interesting consequence of our theory. The experimental results obtained by the senior author on blue light at low intensities, are interpreted on the present theory as indicating that the diffusivity of the transmitting medium is a constant for those conditions. Now, if the diffusivity becomes constant there is nothing to bring the critical speed back to zero when the opening becomes small. Consequently the speed should continually increase with decreasing angle. The actual shape of the curve for illuminations below which the critical speed is independent of the illumination is obtained by making the term within brackets in the above equation constant, choosing an experimental 180-degree value. No relationship of this character between critical speed and angular opening has been observed before, so that its existence or non-existence forms a severe test of the new theory.

The straight lines *d* are the critical frequency-log I lines as predicted for various openings. It will be noted that they are of different slopes, the slope varying continuously with the angle. As a consequence, the curves showing the relationship between angular opening and speed are unsymmetrical to different degrees at different illuminations, as shown also by curves *a* and *b*.
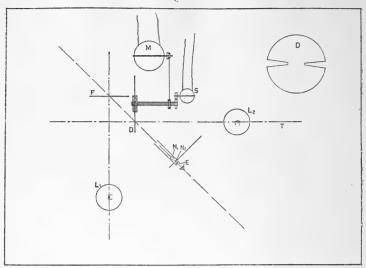
The experimental study of these points is described in the next section.

(b) *Experimental.*

The apparatus used in all the experimental work described in this paper is shown diagrammatically in fig. 5. L_1 and L_2 are point source "100 candle-power" carbon lamps, L_1 being fixed and L_2 movable along a photometer track T. F is a white surface of magnesium oxide on which falls the light from the lamp L_1. D is a sector disk of the form shown in the separate sketch at the side whose purpose is to interrupt the view of the surface F when the apparatus is used for critical frequency studies, and to receive the light from the lamp L_2 when the apparatus is used as a flicker

photometer. In the former case the disk need be merely opaque, in the latter case it must have carefully bevelled edges and be evenly covered with magnesium oxide. A series of disks having various openings were provided, several

Fig. 5.

Plan of Experimental Apparatus.

L_1, L_2, light sources.   M, motor to drive disks.
T, photometer track.   S, electric speed-counter.
F, white surface.   E, observing aperture.
D, sector disk. N_1, N_2, Nicol prisms.

being arranged for use with the flicker-photometer arrangement, the majority, however, being simple thin opaque disks of metal not whitened. These latter were used exclusively in the critical frequency experiments. M is the electric motor used to drive the disk. Its speed is regulated by a series resistance and read upon an electric speed-counter S. The latter consists of a small toy motor (provided with disproportionately large and close-fitting brushes) used as a generator, its E.M.F. being measured on a millivoltmeter. This speed-counter was calibrated by stop-watch and revolution-counter and found to give an accurately rectilinear speed-voltage relation. E is the observing aperture, of one square millimetre area. N_1 and N_2 are Nicol prisms, by means of which the brightness of the observed field can be varied over a wide range. The effective area of the field of view has a diameter of about $9\frac{1}{2}$ degrees.

Details of the method of observation were quite similar to those employed in an earlier investigation to which reference may be made *.

The first point to be studied was the shape of the curve connecting critical frequency and angular opening. This was investigated by obtaining the critical speeds for a series of opaque disks whose openings were 30, 120, 180, 240, 300, 330, and 345 degrees. The experimental values are shown in fig. 4 along with the computed ones. Two sets are

Fig. 6.

Critical frequency-log I data for 30° and 330° degree white disks, showing absence of symmetry at all illuminations.

shown, one set, for a comparatively high illumination, exactly as obtained, a second set for a lower illumination, derived from the others from critical frequency-log I data to be discussed presently.

It will be seen that the computed and observed data are, in general, similar. The chief difference between the expression used by Porter to represent this case and the one

* "Spectral Luminosity Curves obtained by the Method of Critical Frequency," Ives, Phil. Mag. Sept. 1912, p. 352.

used by us is that ours calls for a lack of symmetry about
the 180-degree axis. This lack of symmetry appears in the
experimental results, and, being a point of some importance,
we have established it with some care by a series of obser-
vations for the complementary openings 30 degrees and
330 degrees over a long range of illumination, as shown in
fig. 6. These observations were made alternately with
each angle at each illumination with complementary opaque
rotating disks.

The next point to occupy our attention was the slope of
the critical frequency-log I lines for various angular openings.
Data obtained by us on several occasions are shown both in
the figure just referred to and in fig. 7. While there are
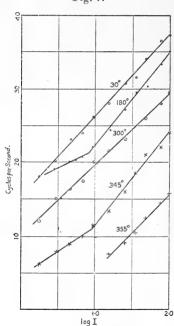
Fig. 7.
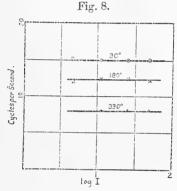
Critical frequency-log I data for various white angular openings,
showing no systematic relation between angular opening and slope. (The
different sets, because obtained under different conditions, are to be com-
pared only for slope, and not for relative magnitude of frequencies.)

differences in the slope of certain of these lines, and while
as well the region covered by experiment is too short to
establish the presence or absence of some systematic difference
of slope, it is clear that there are no such variations of slope

as are called for by our theory as it has been worked out here. The various straight lines are very nearly parallel. Discussion of this discrepancy between our theory and experiment will be reserved till the next section.

The third point studied was the behaviour of the eye toward blue light at low intensities, for different sector openings. The blue light was obtained by the use of a monochromatic blue filter placed over the eyepiece, and the illumination was lowered until the field appeared no longer coloured, but grey. Observations were then made for three angles, 30, 180, and 330 degrees, for four illuminations. The resultant horizontal straight line plots of the data are shown in fig. 8. The approximate symmetry which holds

Fig. 8.

Critical frequency-log I data for blue light at low intensities, for exposures of 30°, 180°, and 330°.

at high illuminations has entirely disappeared. These data are plotted as well in fig. 4 along with the points prophesied from the theory. It is evident that the new phenomenon indicated is a reality, for the critical speed increases continuously as the opening is decreased, instead of returning toward zero as it does for higher illuminations.

(c) *Discussion.*

The conflict between our theory and the data on the slope of the critical frequency-log I lines for various angles is perhaps due to the simplifying assumptions which we found necessary in order to handle the case at all. We have, in fact, used practically the case of a simple sine function superposed on a steady stimulus, and this, as we have already seen (Section 3), gives both from the theory and by experiment, lines of slope varying with the relative magnitude of

the two illuminations. It is to be noted, also, that besides using only the first two terms of the complete expansion, we have made the simplest possible assumption as to the relation between the diffusivity and the amount of light entering the eye. We have as well assumed the Fechner fraction to be the same, no matter what the shape of the transmitted impression. It may very well be that in place of the constant δ some function of the angular opening should be used. Whether these various possible explanations of this discrepancy are sufficient we have not been able to establish. It appears probable to us that, in the simplified form of the theory as worked out, differences actually existing in the slopes of these lines have been much exaggerated. This is a point which can be settled only by the complete solution of the equation from which ω is obtained. We suggest that this might be obtained experimentally by studying the conduction of heat through slabs of various thicknesses, the heat being applied periodically in a manner to imitate the intermittent exposures here studied.

In spite of the apparent disagreement between theory and experiment on this one point, we think it may be claimed that the theory does give the principal facts in a sufficiently striking manner to warrant its being considered as substantially correct. We have felt justified in using it in the remainder of this paper, with the sole caution of confining ourselves to illumination values at which its indications are close to the experimental data.

With regard to the newly discovered behaviour of the eye at low illuminations toward various angular openings, we suggest that it would be an interesting experiment to make measurements with various openings on a totally colour-blind observer. If the behaviour of the eye toward blue light which has become colourless at low illuminations is similar to that of the totally colour-blind eye at normal illuminations, as appears established from various researches, then it is to be expected that with such eyes critical frequency will

    (1) be independent of the illumination ;

    (2) depend upon the opening of the sector, and will decrease as the sector opening is increased.

Von Kries and Uhthoff [*] have made critical frequency

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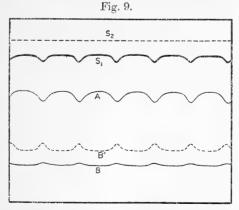
[*] " Ueber die Wahrnehmung des Flimmerns durch normale und durch total farbenblinde Personen," Von Kries, *Zeit. fur Psych. und Phys. der Sinnesorgane,* vol. xxxii. p. 113 (1903).

measurements on a totally colour-blind observer (Uhthoff), and found that the critical speed for him was far below that for a normal observer and seemed little affected by varying the illumination. Unfortunately their account is very meagre of exact data, and they appear to have discontinued the experiments after merely establishing that there is a difference between the two classes of observers.

5. *The Flicker Photometer with Unequal Exposures of the Compared Colours.*

In the design of the flicker photometers a question apt to require answer is, What effect, if any, is to be expected from an unequal exposure of the two fields? An illustrative case is furnished by those flicker photometers which alternate the two fields by the oscillation of a lens or mirror. If the amplitude of the oscillation is small, one side of the field is exposed for a majority of the time to one colour, the other side for a majority of the time to the other colour. Again. if the mechanical centre of the alternating system does not coincide with the optical dividing line unequal exposures result. What will be the effect on the readings?

A qualitative answer to this question is furnished on the basis of our fundamental assumptions by consideration of fig. 9. Here are represented two complementary dovetailed

Fig. 9.

Diagrammatic representation of behaviour of Flicker Photometer with unequal exposures of the compared colours. A and B represent the transmitted stimuli as given by two complementary openings. These have approximately the same fractional range. Their dovetailed summation S_1 shows outstanding flicker. On increasing B to B', the amplitude of fluctuation is increased not only in the proportion of B' to B, but still more due to the increased diffusivity. The new summation S_2 is constant.

impressions as transmitted to the receiving apparatus. Each is due to the same illumination (by different colours) acting on complementary disks. The critical speed is nearly the same for each, consequently the fractional range of each is nearly the same. This, however, means that the actual range is much less for the disk of small opening than for the disk of large opening. The summation of the two impressions is not therefore constant, but partakes more of the nature of the impression due to the larger opening. In order to make the summation constant it is obvious that the illumination of the smaller disk must be increased, whereby the range of fluctuation of the impression due to it will be made larger, and at the same time the diffusivity proper to its colour will be increased, which will assist to the same end.

It follows from this reasoning that that colour of two under comparison which is exposed for the shorter time will be under-rated.

An important point to notice is that this condition holds only if each colour under comparison preserves its individuality to some extent in the process of transmission, as it would do if its transmission is due to a separate mechanism (*e. g.* set of nerves). It is only by this means that the two complementary impressions can be assigned different diffusivities and consequently different ranges. In the case of no colour difference the two impressions must be transmitted by the same channel and the diffusivity must be the same for both—that due to the mean illumination. When the illumination is the same on both sides of such an unsymmetrical flicker photometer the two impressions will exactly dovetail, with a constant summation, which is obviously the case.

This point has bearing on the question of the exact computation of the flicker photometer's behaviour with different colours. We cannot assume that each separately distinguishable colour has its own channel. Three-colour vision theory would point to three such channels as probable. We must therefore expect that the diffusivity governing the transmission of each colour is, to a greater or less extent, modified by the other colour under comparison. This means that such computation as can be made on the basis of each colour having its own diffusivity can be expected to be only qualitative. In the previous paper we have confined ourselves to such qualitative study of the effects of different colours, and a similar restriction holds with the following discussion of the effects of unequal exposures with different coloured lights.

As in the earlier paper, we may calculate the position of setting of the flicker photometer by equating the two ranges, as given by equation (10). Doing this we obtain the equation

$$\log I_1 - \frac{F}{\sqrt{a_1 \log I_1 \phi + b_1}} = \log I_2 - \frac{F}{\sqrt{a_2 \log I_2 (1-\phi) + b_2}} \quad (14)$$

(assuming the substantial correctness of the relation used to connect diffusivity and illumination), where F, a_1, a_2, b_1, b_2 are constants.

Inspection of this equation shows that, as was the case with different colours equally exposed, the first term on each side becomes relatively more important the higher the illumination, that is, the position of setting becomes more and more nearly the equality of brightness point. But in the present case the practical coincidence with the equality of brightness setting is pushed to very much higher illuminations.

We have taken numerical values for red and blue light from the second of the series of papers on the experimental work on the flicker photometer * and inserted them in the equation (14), with the result shown in fig. 10. It is evident
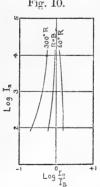
Fig. 10.

The Flicker Photometer with unequal exposures of the compared lights. Relative " slit widths " as calculated for different relative exposures of red and blue light, for different illuminations, showing underexposed colour to be under-rated.

from these curves that, if each colour acted on entirely separate channels, unsymmetrical flicker photometers would read very differently from the symmetrical one, the difference amounting to from 20 to 50 per cent., even at high illuminations.

* " Spectral Luminosity Curves obtained by the Method of Critical Frequency," Ives, Phil. Mag. Sept. 1912, p. 352.

We have confined our verification of the theory to a careful series of unsymmetrical flicker-photometer measurements on green *versus* "white" light, the green (furnished by a pot-green glass over the "white" light) being exposed for 330 degrees, the "white" for 30 degrees. We first made a measurement with two 180-degree exposures with no colour difference, then with the green glass in place, thus determining the transmission of the green glass. The working illumination was maintained constant, and the measurement with no colour difference was made in order to eliminate any errors due to lack of symmetry in the surface of the rotating disk—a matter which will be dwelt on at length in the next section. A 330-degree white disk was then put in place of the 180-degree disk which formed the rotating part of the symmetrical arrangement and exactly the same procedure gone through, giving a new value for the transmission of the green glass. Our results were as follows :

H. E. I. $\dfrac{\text{Transmission with 330 degrees green exposure}}{\text{Transmission with 180 degrees green exposure}} = 1 \cdot 053$

E. F. K.   do. $= 1 \cdot 034$

These figures, showing an over-rating of the longest exposed light, are in agreement with the theory. The amount of this over-rating is less than would be calculated on the assumption of separate channels, but this, as we have shown, is to be expected.

There remains to be considered the question of the sensibility of the unsymmetrical flicker photometer. This we may study in exactly the same manner that we have studied the symmetrical case—by finding and plotting the critical speeds for various relative intensities of illumination from the two compared colours. For this purpose we use the equation
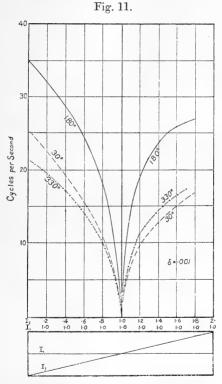
$$\omega = \frac{2\left[\log \dfrac{I_1 - I_2}{I_1\phi + I_2(1-\phi)} + \log \sin \pi\phi - \log \delta\right]^2}{\dfrac{X^2}{K}(\log e)^2}, \quad (15)$$

obtained by combining the range equations for the two exposures. In fig. 11 are shown curves giving the calculated values for the critical speed where one illumination is held constant, the other varied, the constant illumination being exposed for 180 degrees, 30 degrees, and 330 degrees,

as indicated on the respective curves. All values are calculated from the experimental value of 35 cycles per second for the 180-degree case, using the value -3 for $\log \delta$.

These curves show clearly one point which appears at once on experiment, namely, the lower sensibility of the unsymmetrical instrument. There is, too, a somewhat greater lack of symmetry about the equality point than with the equal exposure arrangement.

Fig. 11 exhibits as well in convenient form the phenomena

Fig. 11.

Calculated sensibility characteristics of Flicker Photometer with unequal exposures of the compared lights. One fixed, one variable illumination. Variable illumination exposed 30°, 180°, 330°.

visible in a flicker photometer in which the alternation of the two lights is performed by an oscillating lens or mirror whose excursions are too short. While the centre of the field of such an instrument is equally exposed to the two lights, one side is exposed longer to one light than the other,

and *vice versa*. The three curves of the figure then represent the centre and two sides of such a field. At any given speed flicker disappears, as the illumination from the varying light is increased, first on the large-angle side, then on the small-angle side, then in the centre. Effects of this sort have been noticed by experimenters.

6. *Some Effects of Accidental Dissymmetry on the Critical Frequency and Flicker Photometer Phenomena.*
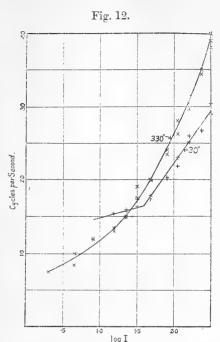
Insistence has been made in previous papers on the importance in the flicker photometer of avoiding all mechanical flicker, such as that from black dividing lines between the alternated fields. One of the most important experimental results of the present work, and one largely unexpected, has been to show in definite quantitative form the extreme seriousness of any sort of lack of symmetry in the flicker photometer. In fact, we believe that many of the contradictory results obtained by experimenters are to be traced back to negligence in the important precautions of securing the greatest possible freedom from mechanical imperfections and in using a strictly substitution method of observation.

The manner in which these effects were discovered offers the best way of presenting them. It was our original intention to test the symmetry of the curve connecting angular opening with critical frequency by alternating observations, first on the illuminated rotating disk and then on the illuminated surface F (fig. 5) as interrupted by the same disk. By first equating the brightness of the disk and white surface through the use of the disk edge to form an equality photometer, it was thought that this alternate measurement with one light and then the other would furnish the best possible test of the symmetry of the effects of complementary disks.

The result of our first series of measurements so made, with a disk of 30 degrees opening, is shown in fig. 12. While the points obtained using the disk merely as an opaque interrupter plot in the normal straight line form, those obtained with the whitened disk fall on a well-marked curve, partly above and partly below the straight line.

The physical cause of this peculiar difference was at once found to lie in the imperfect smoking of the disk with magnesium oxide. A careful re-smoking practically cured the trouble. But so much uncertainty appeared to us to be possible as the character of the white surface varied with

time and use, that this particular alternating method of observation was abandoned. Instead, complementary opaque disks were used as described to interrupt the view of a stationary surface of the best attainable uniformity.

Fig. 12.

Illustrating spurious critical frequency-log I relations obtainable with mechanically imperfect rotating disks. 30° data obtained with opaque disk of 30° opening exposing fixed white surface. 330° data from 330° white disk having surface irregularities. True characteristics of these openings shown in fig. 6.

The explanation we believe to lie in a combination of the phenomena of visual acuity with those of perception of flicker. The disk in its imperfectly smoked state had upon its surface various small specks, brush marks and other irregularities. At high illuminations these defects are most visible, calling for a considerable speed to cause their disappearance. With decreasing illumination and the falling off of visual acuity these defects became less visible and the speed called for approximates that demanded by uniform disks. Whether or not this is the complete explanation, the remedy suggested by it succeeds, and suggests that the method of experimenting with illuminated rotating white

disks should be avoided in favour of opaque disks over a white background, where such troubles are absent.
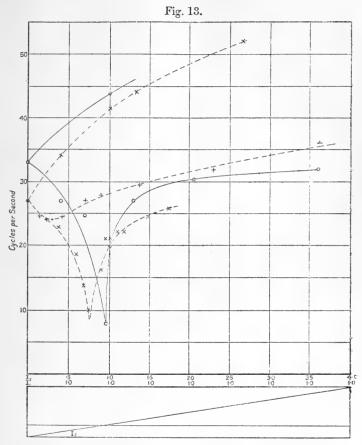
Another serious effect of accidental dissymmetry was found in our experiments upon the flicker photometer with unequal exposures. In passing over from measurements with equal exposures to ones with a ratio of 11 to 1, as described under the previous section, it was found that the flicker setting *with no colour difference* was changed by as much as 15 per cent. The correct setting with no colour difference *must*, of course, be the same with all openings, since it is the same as the equality of brightness or non-flicker setting.

Here, again, it was found that the fault lay in non-uniformities of the rotating-disk surface. Some of the experimental results obtained in searching for the explanation are shown in fig. 13. First of all consider the points marked by circles. These were obtained with a carefully smoked 180-degree disk. The centre line is the equality of brightness point as obtained by using one edge of the disk. It will be seen that the flicker settings are displaced, as a whole, slightly to the left from this centre line. After these readings were made one of the 90-degree sectors of the rotating disk was unsmoked, that is, the magnesia was rubbed off, leaving only the white paint base, of probably 10 per cent. lower reflecting-power. Critical speed readings were then made as before, with the rather striking result of showing that *no minimum of flicker was present*. In short, the arrangement could no longer be used as a flicker photometer. The critical speed for the disk unilluminated was as before (necessarily) 32·5 cycles per second, from which it rose uniformly, being 42 cycles per second at the equality of brightness point of setting.

The points marked by crosses show the more extensive data obtained from the 330-degree white disk with which the effects were first noticed. The lowest curve shows the points found, using a very carefully smoked disk. The speed at the minimum of flicker is quite high, and the median of the figure is much displaced from the point which would have been selected by equality of brightness setting at one edge. (The equality of brightness setting is probably of little significance owing to the small portion of the total disk which figures in making that setting.) The next curve above this, which of course starts from the same point at the left of the diagram, was obtained from the same disk resmoked in an attempt to better the surface. Actually the condition was made worse, as shown by the result. The speed at the minimum is much greater, and the minimum

is 75 per cent. different from the equality setting. The uppermost curve was that obtained upon unsmoking one of the 165-degree sectors of the 330-degree disk. There is now no minimum at all.

Fig. 13.

Experimentally determined Flicker Photometer sensibility character-istics using sector disks of imperfect uniformity of surface. Circles : 180° white disk; crosses: 330° white disk; with various amounts and evenness of magnesium oxide smoking.

It is of considerable interest to find that our theory accounts in a quantitative way for these phenomena of mechanical asymmetry. Let us take, as the simplest case, a 180-degree white disk, composed of two 90-degree sectors, rotating in front of a fixed white surface, the disk and surface being illuminated by separate light sources to the same intensity.

If there are no mechanical irregularities whatever, the speed necessary to eliminate flicker on the alternation of the two surfaces by the rotation of the disk is zero. Suppose, now, the reflecting-power of one of the 90-degree sectors is reduced by ten per cent. From equation (15) we obtain at once that the critical speed at what was the no-flicker point, due to a 90-degree sector of 9/10 illumination, is raised to about 12 cycles per second (using the value ·001 for δ). Now comes an interesting point. The computation as made applies to a disk similar to those for which all the data were obtained, namely in which the 90-degree sector is actually two 45-degree sectors. In other words, our speed counter being calibrated to read twice the actual number of rotations, it follows that the speed called for by the above computation must be *doubled* to make flicker disappear, or 24 cycles are called for. (For smaller values of δ this speed is considerably higher.) Similarly, any single spot or other irregularity exerts a two-, four-, or more-fold disturbing effect according as the rotating disk is composed of two, four, or more sectors, for its period is reduced in that proportion with respect to the period of alternation of the illuminations. This multiplying effect would, of course, be reduced to a minimum by the use of a single sector in place of the two as here used, an arrangement more difficult mechanically.

The computation just made applies to the equality point as determined before the one sector is darkened. The computation of intermediate positions, where the field presents three different degrees of brightness in succession, is not capable of treatment by the theory in its present state of development. The theory has, however, served its purpose in showing how the most striking effect, namely, the very great increase of critical speed at the mid position, is brought about by mechanical defects. The facts found by experiment are thus in accord with the theory, although here, as has happened before, the actual phenomena are of that exaggerated magnitude which call for surprisingly low values of the Fechner fraction.

Escape from the effects of irregularities of this sort lies primarily, of course, in the mechanical symmetry of the apparatus. But no matter how perfect the flicker photometer, it is evident that a strict substitution method of measurement should be adhered to. A mechanically imperfect flicker photometer has its own individual setting for lights of the same colour, which may be considerably different from that of the same or another instrument used on the same photometer track as an equality instrument.

This setting for no colour difference should always be determined.

It is our belief that a number of anomalous results which have been obtained and reported in the use of the flicker photometer are to be traced to asymmetric conditions such as those just discussed. We may note among these :—

First : Comparison of the readings of flicker and equality of brightness photometers. Measurements of a colour difference have been made first with an equality photometer and then with a substituted flicker photometer, with surprising differences. Such readings should always be compared against the reading of the same instruments with no colour difference present.

Second : Comparison of the readings of a flicker photometer which exposes each field equally with ones in which one colour is exposed longer than the other. Very large differences between such photometers have been reported, contrary to our findings reported above. Here, again, the no-colour-difference setting should be determined for each instrument and taken as the starting point.

Third : Comparison of the areas of spectral luminosity curves obtained by the flicker and equality of brightness methods. These have been frequently found to differ, although the shapes of the curves are, under certain conditions, the same. These differences may, in part, be real, but the curves, as obtained by the senior author [*], were determined under conditions which would readily permit the occurrence of dissymmetries of the kind which have been discussed, and whose effect would be to cause area-differences of just the kind found. The conclusions drawn as to the generality of these area-differences may therefore be modified. In the experimental determination of the equality of the sum of the parts to the whole, with the flicker photometer [†], which was the only case where the exact measurement of areas was of vital significance, most elaborate precautions were taken to obtain a photometric arrangement free from any mechanical irregularities, the importance of this being recognized from general considerations.

We have dwelt at considerable length on these effects of accidental dissymmetry because it is important that their nature be understood and the necessary precautions taken

* "Spectral Luminosity Curves obtained by the Equality of Brightness Photometer and the Flicker Photometer under Similar Conditions," Ives, Phil. Mag. July 1912, p. 149.

† "The Addition of Luminosities of Different Colour," Ives, Phil. Mag. Dec. 1912, p. 845.

to avoid them. It must not, however, be gathered that their occurrence renders the flicker photometer an unreliable or troublesome instrument. It is quite as easy to use it properly as improperly.

7. Summary.

While the primary purpose of this paper and the preceding one has been to develop a theory to explain previously ascertained experimental facts, the new experimental results—called forth by the predictions of the theory and the wish to verify all the consequences—are sufficiently valuable to demand that the summary be divided into two parts—" experimental" and " theoretical."

Experimental.

(*a*) Phenomena of frequency of disappearance of flicker.

1. Different ratios of light to dark exposures under constant illumination call for varying critical speeds. At high illuminations a maximum occurs for approximately equal light and dark intervals, but the curves connecting relative period of light exposure and critical speed are not symmetrical.

2. At low illuminations, using blue light, the maximum at equal light and dark exposures is absent. Instead the critical speed increases continuously as the ratio of light to dark interval is decreased.

3. The relationship between illumination and critical speed is represented by the equation

$$\text{critical speed} = a \log \text{illumination} + b,$$

where "*a*" and "*b*" are constants, "*a*" being closely the same whatever the relative light and dark exposures, and "*b*" varying with the relative exposure.

4. When a flickering illumination is superposed on a steady one, the critical frequency is connected with the mean illumination by the same logarithmic relation as that just given, but the constant "*a*" varies with the ratio of flickering to steady illumination.

(*b*) Behaviour of the flicker photometer.

5. The high sensibility of the flicker photometer is shown to be due to the very rapid increase in the critical frequency of disappearance of flicker on each side of the equality setting.

6. In a flicker photometer which exposes the compared colours for unequal periods, the less exposed colour will be

under-rated. This form of flicker photometer is less sensitive than the ordinary equal exposure arrangement.

7. Mechanical imperfections in the flicker-photometer field are shown to seriously shift the equality point even with no colour difference, emphasizing the necessity for strictly substitution methods in flicker photometry.

Theoretical.

The behaviour of the visual apparatus toward intermittent light is closely parallel to the action of a layer of matter, obeying the Fourier conduction law, in which the diffusivity varies as the logarithm of the intensity of the illumination, this layer being exposed to the intermittent light on one side, while its condition on the other side is measured by an instrument whose sensibility is governed by the Weber-Fechner law.

Or, given the experimental data on the behaviour of the eye in perceiving flicker with equal dark and light sectors for different colours at various intensities, it is possible from the most general law of conduction, on the basis of the simple assumptions here made, to predict with considerable accuracy the phenomena occurring with disks of varying openings, at both high and low illuminations, the phenomena with superposed flickering and steady illuminations, the sensibility characteristics of the flicker photometer, the behaviour of the flicker photometer toward different colours at various illuminations, the occurrence of colour flicker and brightness flicker, the effect of unequal exposures of the coloured lights under comparison, and the disturbing effect of mechanical defects in the photometric field.

The phenomena explained or predicted by the theory constitute, in fact, all the known experimental facts in connexion with the flicker photometer. Where the correspondence between theory and experimental fact is more qualitative than quantitative, we have advanced reasons for believing these differences to be due to the approximate nature of the solutions given of the mathematical work, or the insufficiency of our experimental knowledge of certain factors.

Physical Laboratory,
The United Gas Improvement Company,
Philadelphia, Pa., Oct. 1915.

XXXVII. *Theory and Experiments relating to the Establishment of Turbulent Flow in Pipes and Channels. By* LOUIS VESSOT KING, *M.A.(Cantab.), D.Sc.(McGill), Associate Professor of Physics, McGill University, Montreal**.

INDEX TO SECTIONS.

PART I.

THE MATHEMATICAL THEORY OF VISCOSITY AND ITS EXPERIMENTAL VERIFICATION.

Section 1. *Historical Survey of the Theoretical Development.*

AS the fundamental problem of fluid-resistance in both laminar and turbulent flow is intimately connected with the mechanism of shearing stresses across adjacent layers of a fluid in relative motion, it may not be out of place in the present paper to undertake a critical survey of the theory of viscosity and of its experimental verification. The fundamental hypothesis of viscosity asserts that when layers of a viscous fluid are in motion relatively to each other, the mutual tangential stress per unit area is proportional to their relative velocity divided by the distance between them. To be more precise, suppose the fluid to be flowing in layers parallel to the plane xy with velocity U in the direction of the x-axis. If the gradient of velocity in the direction of the z-axis be dU/dz, the shearing stress per unit area of the plane xy in the direction of flow is given by

$$F = \mu \frac{dU}{dz}, \qquad \cdots \cdots \quad (1)$$

μ being a constant depending only on the physical properties of the fluid and called the "coefficient of viscosity."

The insertion of the fundamental hypothesis (1) in the

* Communicated by the Author.

general scheme of hydrodynamical equations seems to have first been effected by Navier [1] and Poisson [2], the justification for this procedure resting on theoretical considerations as to the mutual interactions of the ultimate molecules of fluid.

Since dU/dz represents the rate at which shearing strain is produced by the shearing stress, the hypothesis (1) may be expressed in the language of elastic solid theory by saying that the ratio of the shearing stress to the rate at which shearing strain is produced is equal to μ, the coefficient of viscosity. From this point of view the familiar equations of viscous-fluid theory were developed by Saint-Venant [3] and Stokes [4] ; from this mode of presentation it appears that (1) is the simplest hypothesis consistent with the linearity of the general equations.

The experimental justification of the accuracy with which the fundamental hypothesis is able to give an interpretation of reality rests on the comparison of a comparatively small number of simple experimental conditions of viscous flow with the theoretical solutions. Some of these will now be considered in the following sections [5].

Section 2. *Steady Motion between Parallel Planes.*

The origin is taken half way between the planes and the velocity U is measured along the axis of x parallel to the planes, while the axis of y is taken perpendicular to the planes. If $\partial p/\partial x$ is the pressure-gradient along the axis of x, the equation of steady motion is [6]

$$\mu \frac{\partial^2 U}{\partial y^2} = \frac{\partial p}{\partial x}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As long as the flow is laminar there is no component of velocity parallel to the y-axis, and $\partial p/\partial x$ is an absolute constant given by

$$\partial p/\partial x = (p_2 - p_1)/l, \quad . \quad . \quad . \quad . \quad (3)$$

where $p_2 - p_1$ is the pressure-difference between two points at a distance l apart. Assuming that the coefficient μ is an absolute constant depending only on the properties of the

[1] Navier, *Mém. de l'Acad. des Sciences,* t. vi. p. 389 (1822).

[2] Poisson, *Journ. de l'Ecole Polytechn.* t. xiii. p. 1 (1829).

[3] Saint-Venant, *Comptes Rendus,* t. xvii. p. 1240 (1843).

[4] Stokes, Trans. Camb. Phil. Soc. vol. viii. p. 287 (1845); Math. and Phys. Papers, vol. i. p. 75.

[5] A valuable historical and critical account of viscosity is given by Brillouin (Marcel), 'Leçons sur la viscosité des liquides et des gaz,' Gauthier-Villars, Paris, 1907.

[6] Lamb, 'Hydrodynamics,' p. 542 (1906).

fluid and not on the relative velocity of adjacent layers, the general solution of (2) is

$$U = A + By + (1/2\mu) \cdot (\partial p/\partial x) \cdot y^2 \ , \quad . \quad . \quad (4)$$

A and B being constants of integration. Experimental evidence[7] is consistent with the condition $U = 0$ at the boundary $y = \pm b$; under these conditions

$$U = -(1/2\mu)(b^2 - y^2) \cdot (\partial p/\partial x), \quad . \quad . \quad (5)$$

so that the velocity at the centre U_0 is given by

$$U_0 = -(b^2/2\mu) \cdot (p_2 - p_1)/l \quad . \quad . \quad . \quad (6)$$

The total flow per unit breadth is given by the expressions

$$\Phi = \int_{-b}^{+b} U \, dz = -\frac{2}{3}\frac{b^3}{\mu}\frac{\partial p}{\partial x} = -\frac{2}{3}\frac{b^3}{\mu}\frac{(p_2 - p_1)}{l} = \frac{4}{3}bU_0, \quad (7)$$

and the mean velocity is thus given by

$$\overline{U} = -\tfrac{1}{3}(b^2/\mu) \cdot (\partial p/\partial x) = \tfrac{2}{3}U_0 . \quad . \quad . \quad (8)$$

This simple case of steady motion has been made the starting point of some of the various theoretical treatments of the stability of laminar motion briefly reviewed in Part II. As far as the writer is aware, no experiments have been carried out with a disposition of apparatus corresponding to this solution. As the linear hot-wire anemometer developed by the writer and described in detail in a previous paper[8] is especially suited to the study of this distribution of velocities, the present solution was made the basis of a detailed experimental investigation of gaseous viscosity by studying not only the variation of the total flow with pressure-gradient, lengths and breadths of channels, &c., but by an actual examination of the gradients of velocities themselves. The high resolving-power and sensitiveness to low velocities of the linear hot-wire anemometer make this instrument exceptionally useful for this type of work. The results obtained by this means (which will be fully illustrated

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[7] See Lamb, 'Hydrodynamics,' p. 544. In the case of gases, recent experimental work by Knudsen ('La Theorie du Rayonnement et les Quanta,' Gauthier-Villars, Paris, 1912, p. 133 *et seq.*) and by Dunoyer ('Les Idées Modernes sur la Constitution de la Matiere,' Gauthier-Villars, Paris, 1913, p. 215 *et seq.*) on ultra-rarefied gases indicates that molecules actually embed themselves in the material of the boundary, to return into the gas at some later time with a velocity whose direction is entirely independent of the previous collision with the walls.

[8] King, L. V., "On the Precision Measurement of Air Velocity by means of the Linear Hot-Wire Anemometer," Phil. Mag. vol. xxix. April 1915, pp. 556–572.

and discussed in Part III.) indicate the somewhat surprising result that the parabolic distribution calculated from the usual viscous fluid theory is only a rough approximation to a much more complicated state of affairs.

Section 3. *Steady Motion in a Pipe of Circular Cross-Section.*

Taking the axis of z to coincide with that of the circular cylinder, the pressure-gradient in this direction is constant and is given by

$$\partial p / \partial z = (p_2 - p_1)/l, \quad . \quad . \quad . \quad . \quad (9)$$

$p_2 - p_1$ being the pressure-difference measured at points a distance l apart. The equation for steady motion is [9]

$$\frac{\partial}{\partial r}\left(\mu r \frac{\partial W}{\partial r}\right) = -r(p_2 - p_1)/l, \quad . \quad . \quad . \quad (10)$$

of which the general solution is

$$W = -r^2(p_2 - p_1)/(4\mu l) + A \log r + B \quad . \quad . \quad (11)$$

Under conditions of finite velocity along the axis $r = 0$ and no slipping at the boundary $r = a$, we have

$$W = (a^2 - r^2) (p_2 - p_1)/(4\mu l). \quad . \quad . \quad . \quad (12)$$

The maximum velocity at $r = 0$ is given by

$$W_0 = a^2(p_2 - p_1)/(4\mu l), \quad . \quad . \quad . \quad . \quad (13)$$

and the total flow is

$$\Phi = \int_0^a W \cdot 2\pi r \, dr = \pi a^4 (p_2 - p_1)/(8\mu l) = \tfrac{1}{2}\pi a^2 W_0, \quad (14)$$

and the mean velocity over the cross-section is

$$W = \tfrac{1}{2} W_0. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This solution forms the basis of most of the practical methods of determining the coefficients of viscosity of a liquid or of a gas; it is also the starting point of some of the theoretical treatments on the stability of stream-line flow, and, until the writer's own experiments on the subject, all observations on the laws of flow were confined to the case of pipes of circular cross-section. It is generally assumed that the theory of viscosity obtains its application to reality in that equation (14) contains all the laws found experimentally by Poiseuille [10]; although these laws have been

[9] Lamb, 'Hydrodynamics,' 1906, p. 543.
[10] Poiseuille, *Comptes Rendus*, vol. xv. p. 1167 (1842).

amply verified in the case of tubes of capillary diameters, a marked deviation is easily noticeable as soon as the diameters exceed a few millimetres, even at velocities considerably below what is taken to represent the "critical velocity."

Section 4. *Shearing Motion between Parallel Planes.*

Measuring y perpendicular to the moving planes at a distance d apart, the equation for steady motion is $d^2U/dy^2 = 0$, of which the solution appropriate to $U = 0$ at $y = 0$, and $U = U_0$ at $y = d$ is

$$U = U_0 y/d, \quad \ldots \quad \ldots \quad (16)$$

which, it will be noticed, does not involve the viscosity. The shearing stress between the planes per unit area is

$$F = \mu(dU/dy)_0 = \mu U_0/d. \quad \ldots \quad \ldots \quad (17)$$

In this case experiment measures the shearing stress F ; it may be remarked here that in these circumstances the fundamental law of viscosity relates to the traction between the fluid and a solid boundary and not to the traction between layers of fluid, as would be revealed by an experimental analysis of the velocity-gradients themselves.

The simple case just considered is not realizable experimentally, although it is made the starting point of one of the important cases of laminar flow examined theoretically from the standpoint of stability. The appropriate experimental arrangements involve the measurement of the tractions between circular disks, as in Maxwell's classical experiments, or between concentric spheres or cylinders ; observations are generally carried out by oscillation methods, although an apparatus has recently been constructed by Gilchrist[11] which enables the torque due to viscous shear between relatively rotating coaxial cylinders to be measured. Taking the case of a cylinder of radius a, rotating with angular velocity ω_0 inside a coaxial cylinder of radius b, the angular velocity in the fluid at radius r is given by[12]

$$\omega r = (a/r) \cdot (b^2 - r^2)/(b^2 - a^2) \cdot \omega_0 a, \quad \ldots \quad (18)$$

while the couple exerted between the cylinders is, per unit length,

$$L = -4\pi \mu a^2 \omega_0 \cdot b^2/(b^2 - a^2). \quad \ldots \quad (19)$$

Gilchrist points out, in a review of the best experimental data available at the date of his paper, that small discrepancies

[11] Gilchrist, Phys. Rev. vol. viii. p. 124 (1913).

[12] Lamb, 'Hydrodynamics,' 1906, p. 546.

of about 0·5 of one per cent. exist in determinations of the coefficient of viscosity by the various methods employed, and that these cannot be attributed to errors of experiment.

As has already been pointed out, measurements of the viscosity of gases carried out by these methods depend on the shear between a solid surface and a gas, the laws for which may not be identical in all circumstances with those relating to tractions between successive layers of gas. Moreover, all these methods entail very low relative velocities and rates of shear, while any slight departures from the theoretically specified motion have generally been attributed to the breakdown of viscous stream-line flow to "turbulent flow" without further examination. Any direct measurements of velocity-gradients do not appear to have been carried out, although this is now possible owing to the development of the linear hot-wire anemometer described in a previous paper by the writer. Any factor other than the viscosity resulting from the free-path transfer of momentum might easily have escaped observation in the type of experiments referred to, as the inertia of the moving surfaces employed would tend to smooth out any extraneous irregularities in viscous tractions which might exist. The writer hopes, at some future date, to undertake the analysis of velocity-gradients in these cases by means of the hot-wire anemometer; it may well happen, as in the case of flow between parallel planes, that factors other than the viscosity due to free-path phenomena may play a part in determining the velocity-gradients and tractions referred to.

Part II.

On the Stability of Laminar Flow in Pipes and Channels.

Section 5. *Historical and Critical Survey of the Theoretical Development.*

The origin of the theoretical work on the subject of the present chapter dates back to Helmholtz's remark that surfaces of discontinuity in perfect fluids are unstable [13]. The subject was treated mathematically at an early date by Rayleigh, especially in connexion with the stability of jets and the explanation of phenomena relating to sensitive

[13] Helmholtz, Phil. Mag. Nov. 1868 ; *Gesammelte Abhandlungen*, i. p. 146 (1882–3).

flames [14]. Osborne Reynolds's experimental work on the
subject in 1883 marks an important point in the history of
the subject [15]. By studying the nature of the flow by means
of colour-bands, it was shown that at a certain " critical "
mean velocity the stream-like flow broke up into violently
eddying motion; it was also shown from the theory of
dimensions that the criterion of breakdown should depend
on the ratio $D\overline{U}\rho/\mu$ only, D being the diameter of the tube,
$\overline{U}$ the mean velocity of the fluid, ρ its density, and μ its
coefficient of viscosity, all these quantities being measured
in C.G.S. units. The passage from laminar to turbulent
flow was indicated both by the colour-band method, as well
as by a change in the law of resistance as observed from
the discontinuity in the curve connecting the total flow and
the pressure-gradient, and was shown to take place for a
value of $\overline{U}$ given by the relation

$$D\overline{U}\rho/\mu = K, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

which will be referred to as "Reynolds's Criterion," while
the number K will be referred to as "Reynolds's Constant."
In the case of water Reynolds found, both from his colour-
band method as well as from a study of his own experiments
and those of Poiseuille [16] and Darcy [17] on the laws of fluid
resistance in pipes, that K had a value in the neighbourhood of
$K = 1900$ to 2000. According to theory K should have the
same value for all viscous *incompressible* fluids. Several
series of observations, carried out since that date by various
observers on liquids and gases, when examined by the same
methods as those employed by Reynolds, agree in assigning
fairly consistent values to the constant K; these are discussed
in further detail in the next section.

Reynolds's observations gave rise to a series of theoretical
contributions, among the first of which were papers due to
Kelvin [18] and Rayleigh [14]. Kelvin examined the types of
flow discussed in Sections 3 and 4 from the point of view
of stability, and came to the conclusion " that the steady
motion is wholly stable for infinitesimal disturbances,
whatever may be the value of the viscosity (μ); but that
when the disturbances are finite the limits of stability

[14] Rayleigh, Various papers between 1879 and 1914; Collected Works,
Arts. 58, 66, 144, 194, 216, 217; also Phil. Mag. vol. xxviii. p. 609,
Oct. 1914.

[15] Reynolds, O., Phil. Trans. vol. clxxiv. p. 935 (1833); Collected
Works, vol. ii. p. 51.

[16] Poiseuille, *Comptes Rendus*, vols. xi. & xii. (1840–1).

[17] Darcy, *Comptes Rendus*, vol. xxxviii.

[18] Kelvin, Phil. Mag. vol. xxiv. pp. 188, 459, 529 (1887).

become narrower as μ diminishes." These views have been criticized by both Rayleigh [19] and Orr [20].

Rayleigh's earliest papers on the subject deal with the laminar steady motion of a perfect fluid between parallel planes in which the distribution of *velocity* is continuous, while the *rotation* or *vorticity* changes suddenly on passing from one layer of finite thickness to the next. Rayleigh's general conclusion is thus stated : " The steady motion of a non-viscous fluid in two dimensions between fixed parallel walls is stable provided that the velocity U everywhere parallel to the walls is such that d^2U/dy^2 is of one size throughout, y being the ordinate measured perpendicularly to the walls. It is here assumed that the disturbance is *infinitesimal*."

The extension of this ideal problem to include the case of an actual fluid possessing viscosity brings us at once to the main (theoretical) difficulty of the subject, and one which cannot yet be regarded as (theoretically) settled. The subject was proposed for discussion in the Adams Prize Essay of 1887, and may be considered to constitute the simplest case of fluid resistance. Many writers, including Reynolds himself [21], have since that date contributed to the theoretical aspect of the subject, and have succeeded by various methods in establishing theoretically determined values of Reynolds's Constant K, for cases of flow which not only include that between parallel planes but also the more difficult one of the circular tube. These are reviewed in an important memoir by Orr [20], who himself gives an original treatment of the subject. An authoritative account of the present state of the problem, from which the writer has quoted the above passages, has recently been published by Rayleigh [22]. It is therefore unnecessary to deal at greater length with this aspect of the subject in the present paper, beyond stating that the most recent theoretical treatment of the subject by Hopf [23], following a method due to

[19] Rayleigh, Phil. Mag. vol. xxiv. pp. 59–70 (1892) ; Collected Works, vol. iii. p. 575.

[20] Orr, Proc. Roy. Irish Acad. vol. xxvii. pp. 9–138 (1907). This important memoir gives a critical account of the theoretical work on the subject to the year 1907 in great detail.

[21] Reynolds, Phil. Trans. vol. clxxxvi. A, p. 123 (1894) : Scientific Papers, ii. p. 535.

[22] Rayleigh, "On the Stability of Viscous Fluid Motion," Phil. Mag. Oct. 1914 ; see also Phil. Mag. Sept. 1915.

[23] Hopf, *Ann. d. Phys.* xliv. no. 9, pp. 1–60 (1914). See also a recent discussion of the subject by Taylor, R. I., Phil. Trans. Roy. Soc. vol. ccxv. A. pp. 23–26 (1915).

Sommerfeld [24], tends to confirm the original conclusions of Kelvin and Rayleigh as to the stability of a state of steady motion.   The unsatisfactory state of knowledge at the present time on the subject is clearly shown from the Table given at the end of this paper, from which it is seen that the theoretical estimates of Reynolds's Constant K differ very markedly from each other, and very greatly from the generally accepted values obtained for liquids and gases.

It may be noted that all experimental data refer to tubes of *circular cross-section*, whereas the simplest theoretical case refers to the flow of fluid between *parallel planes* ; in the latter case observations have not hitherto been available. The deficiency is now made up by the writer's own experiments on the flow of air to be described in detail in Part III. ; the results indicate the existence of hitherto unsuspected conditions of laminar flow, both at extremely low velocities as well as at velocities considerably higher than those which are taken to represent, according to the usual interpretation, critical velocities.

By means of the linear hot-wire anemometer developed by the writer [8], the velocity-distribution over the cross-section of a two-dimensional channel (section 0.45 cm. $\times 5.08$ cm.) was measured for various pressure-differences.   Owing to the high resolving power of the instrument, it was found possible to measure velocities at intervals of 0.05 mm. over the cross-section, and in this way a velocity-distribution curve representing as many as 100 observations could be obtained, the pressure-difference under which the flow took place being maintained constant to $1/10$ of one per cent. Even at velocities considerably below the " critical velocity," as usually defined, the distribution curves showed consistent and interesting deviations from the parabolic form demanded by theory.

(i.) The experimental curves developed well‑marked " humps " in the neighbourhood of planes midway between those dividing the distance between the walls of the channel in equidistant parts ; these appeared at very low velocities (maximum velocity 20 cm. per sec.), and, with increasing velocities, the number of " humps " increased, as many as nine being easily discernible in the curve corresponding to a maximum velocity of 650 cm. per second.

(ii.) Although the general shape of these distribution curves is parabolic, the maximum falls very much below that demanded by the theoretical viscous-flow theory, as

[24] Sommerfeld, Proc. Int. Congress of Mathematicians, Rome, 1908.

though some factor contributed to increase very materially the ordinary kinetic-theory coefficient of viscosity.

As the peculiarity (i.) would seem to associate the phenomenon with transverse stationary sound-waves (in the particular instance quoted the pitch of the gravest mode would be much above audition), it would seem not unnatural to attribute (ii.) to the same cause. Making use of a conception which appears to have been first put forward by Brillouin [25] in another connexion, the "rationale" of the phenomenon would appear to be as follows :—When flow of a *compressible* fluid takes place under conditions which permit of the establishment of stationary modes of sound-vibrations (as in flow in non-capillary tubes, channels, &c.), the wave-front is refracted by the velocity-gradients which exist in the medium. As rate of change of momentum is propagated along a sound-ray, it follows that, under these conditions, the existence of compressional vibrations will result in a component of rate of change of momentum proportional to the velocity-gradient being transferred across an element of surface parallel to the direction of flow. Hence we must write for the viscosity, $\mu = \mu_0 + \mu_s$, where μ_0 is the ordinary viscosity of the kinetic theory, and μ_s is a "quasi-viscosity" due to the existence of compressional waves and is proportional to the *intensity* of the wave-motion. The theoretical velocity-gradients calculated on this theory give a very satisfactory account of the experimental results : the full details of the theory and the comparison with experimental results will be given in Part III. of the present paper.

It thus appears that the gradual modification with increasing velocities of the laminar flow in channels through the interaction of transverse sound-vibrations with viscous tractions is an essential factor in ultimately leading to the breakdown of stream-line motion. It appears to the writer that in the combination of compressional vibrations and shearing-motion lies the origin of a vortex rotation which, as the amplitudes of the sound-vibrations and their frequencies increase, may ultimately result in the formation of *finite* vortex filaments, resulting finally in "turbulent motion" in the generally accepted sense of the word.

As the factor of compressibility, hitherto neglected in theoretical treatments of the stability of laminar flow by Reynolds, Rayleigh, Kelvin, Sharpe, Orr, and others, appears to be of considerable importance in the light of the

[25] Brillouin, L., "Conductibilité calorifique et viscosité des liquides monoatomiques," *Comptes Rendus*, vol. clix. pp. 27–30, July 6th, 1914.

experimental results briefly described above, it is hardly necessary to consider in further detail the various theoretical treatments referred to.   While the condition of incompressibility assumed in these discussions might possibly be justified in the case of liquids (and some evidence seems to point to compressibility as a determining factor affecting stability in this case as well) [26], it is hardly to be supposed that this factor could be entirely ignored in the case of gases.

In the light of the preceding remarks it appears that still another factor may play a part in determining the instability of flow in tubes and channels, that is, the determinateness of the various transverse modes of sound-vibrations which may be set up.   In a two-dimensional channel (or channel of elongated cross-section) the nodes and loops are extremely determinate in position, and we should expect laminar flow to persist to very high velocities.   In the case of a tube of circular cross-section, however, some of the normal transverse modes (*e. g.* those having diameters as nodes) are *indeterminate* in position, and in an actual case would be determined by accidental inequalities on the interior of the tube or by slight departures from circular form.   It would thus appear that in such cases (which include practically all experimental data) Reynolds's Criterion of "sinuous" motion would be decided, not by instability of steady flow in the usual sense, but by the appearance of the first transverse mode having a diametral node.   Relatively to the fluid, these indeterminate modes would tend to twist around, resulting in a state of affairs which, if continued long enough would, in spite of the stabilizing effect of viscosity, result in a complete destruction of conditions of steady flow.   Many phenomena relating to the "critical velocity" are thus capable of explanation; for instance, the "flashing" first observed by Reynolds [27], making use of the colour-band method, *i. e.* a state of "sinuous" motion over a short length of tube followed by a region of stream-line flow.   The effect of the material of the tubes on the critical velocity observed by several experimenters is probably due, for the most part, to the degree of mechanical finish of the interior surface obtainable with the particular substance employed [28].   In the

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[26] See footnote (36).

[27] Reynolds, footnote (15), fig. 16.

[28] According to the ideas developed in the preceding paragraph, it would seem that the acoustic properties of the walls of the tube or channel may not be without influence on the velocity-gradients in the immediate neighbourhood of the boundary.

flow in tubes of large diameter, the velocity-distribution over a particular cross-section is nearly always unsymmetrical with respect to the axis. Then again, if the curves [29] connecting the total flow with pressure-gradient be carefully examined, it will be noticed that slight discontinuous changes of slope can be detected some time before the "critical flow" is reached; the effect in this case is probably due to sudden changes of velocity-distributions resulting from a number of *symmetrical* transverse modes being brought into existence before the first indeterminate mode leading to a complete breakdown of stream-line flow. If this is the correct interpretation of Reynolds's condition of "sinuous flow," it would seem capable of mathematical formulation leading to a more satisfactory explanation of the experimental constant K. Such an investigation would hardly be profitable in the present state of experimental knowledge until the much simpler and more determinate cases of two-dimensional flow have been thoroughly worked out, both experimentally and theoretically.

Section 6. *Discussion of Experimental Results on the Flow of Viscous Fluids.*

(i.) *Liquids.*—Reynolds's original experiments on the subject have already been reviewed in the preceding section, and a possible explanation of several features of the phenomenon discussed. Further experiments along the same lines by Barnes and Coker [30] give additional support to the view that the passage from stream-line to turbulent flow depends on the determinateness of the transverse modes of the compressional vibrations rather than on the instability of steady viscous flow, as generally understood in theoretical investigations on the subject. The observers just mentioned, by exercising extreme care in preventing the formation of eddies in the tank previous to the entrance of the liquid into the flow-tube, were able to obtain stream-line motion for velocities as much as four times as high as that given by Reynolds's Criterion. In some cases, after passing through a state of turbulent flow, stream-lines *reformed at higher velocities*; in such cases a sharp rap on the tube sufficed to break down the motion, which immediately became stable

[29] Such, for instance, as the curves for air obtained by Kohlrausch, K. W. F., *Annalen der Physik*, xliv. p. 297 (1914); and more especially those obtained by Sorkau for water and various organic liquids. (Footnote 36.)

[30] Barnes, H. T., & Coker, F. G., Roy. Soc. Proc. vol. lxxiv. p. 341 (1904).

when the rapping ceased; the phenomenon of reformation of stream-lines at higher velocities was observed both by the colour-band method and by a special thermal method. It was also noted, in passing, that the amount of colour employed had a marked effect on the velocity at which the colour-band broke up. According to the views expressed in the preceding section, the reformation of stream-lines at the higher velocities would correspond to the excitation of symmetrical transverse modes of higher frequency than the indeterminate mode giving rise to the first appearance of turbulent flow [31].

Among the more accurate observations carried out for the distribution of velocity over the cross-section of a circular pipe through which water was flowing, may be mentioned the experiments of Morrow [32]. Measurements were carried out by means of a Pitot tube, and it was found that the distribution-curves changed *gradually* from approximate paraboloidal distributions to those typical of velocities above the "critical velocity."

The scope of experiments of this type was extended by Stanton [33], and recently in an exhaustive memoir by Stanton and Pannell [34]. The distribution of velocities over the cross-sections of a number of circular pipes was accurately determined for air- and water-flow above the "critical velocity" in order to obtain evidence over as wide a range of density and viscosity as possible as to the accuracy of Rayleigh's Principle of Dynamical Similarity to cases involving surface-friction between solid and liquid surfaces. If R be the resistance per unit area, ν the kinematic viscosity of the fluid $(\nu = \mu/\rho)$, and ρ its density, Rayleigh's Principle [35] gives in its application to the particular case considered,

$$R = \rho \overline{U}^2 F(\overline{U}D/\nu), \quad . \quad . \quad . \quad . \quad (21)$$

where D is the diameter of the pipe, $\overline{U}$ the mean velocity

[31] A close examination of Reynolds's curves (Scientific Papers, vol. ii. diagram 1, p. 90) connecting velocity and pressure-gradient indicates the existence of discontinuities at higher velocities than that taken as the critical velocity.

[32] Morrow, Roy. Soc. Proc. vol. lxxvi. A, p. 205 (1905).

[33] Stanton, T. E., Roy. Soc. Proc. vol. lxxxv. A, p. 366 (1911).

[34] Stanton & Pannell, "Similarity of Motion in Relation to the Surface Friction of Fluids," Roy. Soc. Trans. vol. ccxiv. A, pp. 199–224 (1914). See also a discussion of these results by Lees (Roy. Soc. Proc. vol. xci. A, p. 46, Nov. 1914), who derives from these observations accurate empirical formulæ based on the Principle of Dynamical Similarity, expressing the relations between mean velocity and pressure-gradients for the flow of water and air in pipes of circular cross-section.

[35] Rayleigh, see footnote (19).

over the cross-section, and F some function of the variable $\bar{U}D/\nu$. This principle was fully confirmed in its application to pipes of widely different diameters for fluids differing in density and viscosity to the extent represented by air and water. The value of $\bar{U}D/\nu$ corresponding to "critical" changes in the character of the motion is not very sharply defined, but leads to a value of Reynolds's Constant in the neighbourhood of $K=2500$. It does not appear to the writer that the theory of the mode of breakdown from stream-line to turbulent motion, suggested in the previous section as depending on transverse modes of compressional vibrations, is in contradiction with the principles just discussed, except that the form of the function $F(\bar{U}D/\nu)$, and especially the value of $\bar{U}D/\nu$ corresponding to a change in the type of motion, would depend on the form of the cross-section of the tube, but would probably remain the same for geometrically similar shapes as in the particular case covered by existing experiments on circular cross-sections. For this reason it would seem highly desirable to obtain the corresponding data on two-dimensional channels or cross-sections having an elongated elliptical form; it would be expected that the appearance of the "critical" flow would occur at a higher velocity than that given by the usual Reynolds's Criterion, owing to the high degree of determinateness of the transverse modes.

Mention should be made of numerous experiments by Sorkau [36] on the flow of water and of various organic liquids through a short capillary tube (diameter 0·423 mm.: length about 5 cm.). Observations were made of total flow against pressure; although, as has already been pointed out, such observations are not suitable for revealing discontinuities of flow unless they are well marked, the experiments of Sorkau indicate the existence of three distinct régimes of turbulent flow occurring at velocities considerably less than that given by Reynolds's Criterion. Quoting from the last-mentioned reference given below, the value of K for water varies from $K=413\cdot4$ at $4°$ C. to $410\cdot5$ at $25°$ C. Above $25°$ C. the three turbulent régimes are well-marked. Similar results were obtained in the case of various pure organic liquids.

(ii.) *Gases.*—Accurate observations on the flow of gases with reference to a study of the turbulent régime have only comparatively recently been carried out; in such cases the

[36] Sorkau, W., *Phys. Zeit.* xii. pp. 582–595 (1911); xiii. p. 805 (1912); xiv. pp. 147 *et seq.*, 759–766, 828–831 (1913); xv. pp. 582–587, 768–772 (1914); xvi. pp. 97–102 (1915).

curve connecting the pressure-gradient and the total flow is one of nearly continuous curvature, so that a " critical velocity " in the usual sense is not sharply defined unless the velocities and pressure-gradients are large and the diameters of the tubes small.   An elaborate series of experiments under these conditions was carried out by Ruckes[37], who employed capillary tubes of internal diameters between 0·1 and 2·2 mm. at pressures from a fraction of an atmosphere to about 50 atmospheres; Reynolds's Constant, as determined from the curves connecting total flow and pressure-gradient, had values in the neighbourhood of $K = 2000$; in several cases stability continued until velocities corresponding to values of K between 3000 and 8000 were reached, resembling in this respect the observations of Barnes and Coker[30] already discussed. For metal capillaries K had values as low as 400 and 500, a somewhat surprising result, probably due, as has already been mentioned, to the degree of mechanical finish of the interior of the capillaries.

Experiments by Grindley and Gibson[38] on the flow of air through a long lead pipe (108·2 feet long and diameter 0·125 inch) gave a value $K = 2200$.

Among the earliest observations on the distribution of velocity over the cross-section of tubes may be mentioned those of Becker[39], the velocity-measuring device involving the aerodynamic resistance of small aluminium spheres.

Experiments by Fry and Tyndall[40] were carried out by the use of Pitot tubes, and very sensitive manometers specially designed for the purpose ; the curves of velocity-distribution differed markedly from the paraboloidal distribution required by the viscous theory, and, as in Morrow's observations[32], the transition to distributions above the critical velocity was gradual ; the change took place most rapidly in the neighbourhood of a velocity corresponding to a value of Reynolds's Constant $K = 2500$.

Very elaborate observations along these lines have recently been published by Kohlrausch[41] and are worth careful study. Five glass tubes were employed of diameters between 0·76 and 3·6 cm. Several series of curves connecting the total flow and the pressure-gradient are given ; a careful inspection of these curves shows that, while they exhibit a decided

[37] Ruckes, W., *Ann. d. Phys.* vol. xxv. p. 983 (1908).
[38] Grindley & Gibson, Proc. Roy. Soc. vol. lxxx. p. 114 (1908).
[39] Becker, *Ann. d. Phys.* vol. xxiv. p. 863 (1907).
[40] Fry & Tyndall, Phil. Mag. March 1911, p. 348.
[41] Kohlrausch, K. W. F., *Ann. d. Phys.* vol. xliv. p. 297 (1914).

curvature over the range of velocities below the "critical velocity," there exists an indication of a tendency for the series of points to show more than one interval of discontinuous slope; the "critical" flow is not very sharply marked, but a value is assigned corresponding to a value of the "critical constant" in the neighbourhood of $K = 2080$. Distributions of velocities over the cross-section are studied in detail for one of the pipes by means of a Pitot tube; the results indicate a gradual transition of shape from the "streamline" to the "turbulent" distribution, and a close inspection of these curves, even at the lower velocities, shows a tendency for the curves to assume forms similar to those obtained by the writer for two-dimensional flow of air. The observations of Kohlrausch are not sufficiently numerous, nor the resolving power of the Pitot tube method of measuring velocities sufficiently high, to reveal in their full detail the type of distributions observed by the use of the linear hot-wire anemometer.

Perhaps the most remarkable observations on the subject are those of Dowling[42], which show an indication of an approach to the results of the writer. The criterion of a change in the flow distribution was obtained by an ionization method. The most marked change was obtained for a mean velocity giving values of K averaging 2480 for air and 2500 for carbon dioxide; in the case of long thin tubes the values of K were somewhat increased to 3120 and 3080 respectively, and the anomalous effect of metallic tubes was also noted. The most significant result of these observations was the discovery of a second well-marked critical velocity considerably *below* that from which Reynolds's Criterion is established; in fact, many of the curves obtained by Dowling resemble in their general appearance those obtained by the writer, connecting the velocity at a certain point and the pressure-gradient in presenting a succession of well-marked points of discontinuous slope considerably earlier than that which is generally supposed to mark the commencement of the "turbulent" régime.

[42] Dowling, J. J., "Steady and Turbulent Motion in Gases," Roy. Dub. Soc. Proc. vol xiii. p. 375 (1912). In these experiments, air ionized over a short portion of the tube by a radium source, was examined for electrical conductivity by the usual electrometer method at a distant point. The rate of recombination depends on the nature of the velocity-distribution curve in the tube between the ionizing source and the exploring electrode; the electrometer leak is plotted against the mean velocity and the resulting curve gives a remarkably sensitive indication of sudden changes in the nature of the flow.

Table of Theoretical and Experimental values of Reynolds's Constant relating to the Flow of Fluids in Channels and Pipes : $K = D\overline{U}\rho/\mu$.

Flow in Circular Pipes.

	Authority.	Reference.	Method.	Value of K and Remarks.
Theoretical.	Sharpe.........	Trans. Am. Math. Soc. vol. vi. p. 496, 1905.	Theoretical.	470
	Sharpe.........	....	Theoretical.	363 (corrected by Orr).
	Orr	See footnote (20), p. 134, 1907.	Theoretical.	180
Observations on Liquids.	Reynolds ...	See footnote (21), 1883.	Colour-band and pressure-gradient.	1900–2000
	Couette	Ann. Chim. et Phys. (6) vol. xxi. p. 433 (quoted by Orr), 1890.	....	2150
	Barnes and Coker.	See footnote (30), 1904.	Colour-band, pressure-gradient, and special thermal method.	1950 and with precautions as high as 4360.
	Morrow	See footnote (32), 1905.	Distribution of velocity by Pitot tube.	1980
	Stanton and Pannell.	See footnote (34), 1914.	Extensive observations on air and water by pressure-gradient and velocity-distributions.	Principle of dynamical similarity established. $K=2500$.
	Ruckes	See footnote (37), 1908.	Flow in capillaries : pressure-gradient.	2000 and in some cases 3000–5000. Metal tubes 450.
	Sorkau.........	See footnote (36), 1915.	Extensive observations on water and pure organic fluids: pressure-gradient.	$K=413\cdot4$ to $K=410\cdot5$ for water.
Observations on Gases.	Grindley and Gibson.	See footnote (38), 1908.	Pressure-gradient in long lead tube.	2200
	Fry and Tyndall.	See footnote (40), 1911.	Velocity-distribution by Pitot tube.	2500
	Dowling	See footnote (42), 1912.	Ionization method.	2500
	Kohlrausch. .	See footnote (41), 1914.	Pressure-gradient and velocity-distribution by Pitot tube.	2080
	Stanton and Pannell.	See footnote (34), 1914.	See above.	2500

Flow in Two-dimensional Channels.

Theoretical.	Reynolds ...	See footnote (21), 1894.	Theoretical.	517
	Sharpe..	See above.	Theoretical.	167
	Orr	See footnote (20), p. 130.	Theoretical.	117

Note.—The only experiments available on the flow of air in two-dimensional channels are those obtained by the writer by means of the linear hot-wire anemometer; it appears from these observations that there exist a series of critical velocities, of which the more prominent seem to correspond to those calculated by Reynolds, Sharpe, and Orr.

XXXVIII. *Ionic Mobilities in Hydrogen.*—II.   *By* W. B. HAINES, *B.Sc., D.I.C., Beit Scientific Research Fellow*[*].

IN a recent paper[†] the author gave the preliminary results of experiments showing the presence of several kinds of negative carriers in pure hydrogen ionized by α-rays. Experiments have now been made at different pressures, so that a revised and extended series of measurements can be given.
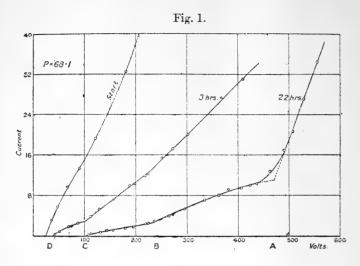
Experimental.
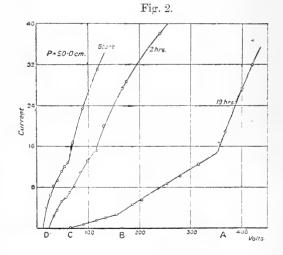
As described in the former paper, the apparatus is so arranged that the ions move under the influence of a simple harmonic alternating field between two metal plates. From readings of the current carried by the ions for different values of the amplitude of the field, the critical value of the amplitude can be found at which the ions just travel the distance between the plates and back in one cycle of the field. A mercury manometer tube was attached to indicate the pressure of the gas in the experimental chamber. Measurements could be conveniently taken between atmospheric pressure and about 8 cm., so that a filter-pump sufficed for lowering the pressure. In order to ensure that the hydrogen should retain a high state of purity at lowered pressures the chamber had to be rendered thoroughly air-tight, which is not an easy matter with different parts of glass, ebonite, and brass held together with sealing-wax. After one or two attempts this was satisfactorily accomplished by covering all the joints, when carefully made with sealing-wax, with a soft wax requiring only a moderate degree of heat to render it quite fluid, so effectively filling all minute cracks and pores.

The method adopted as giving the most consistent results was first to fill the chamber at the pressure desired with pure hydrogen as it comes from the cooled charcoal bulb. The gas was then left standing and at intervals a complete series of readings of current against voltage was taken, so that the changes in the ions which go on as the contamination increases could be observed. In most cases the hydrogen was freshly prepared from zinc and dilute sulphuric acid, but the same results are noticed when the gas has stood for some days in a holder, provided that it is freshly purified

with charcoal before the measurements. The changes which take place in the ions are very large, as will be seen by a reference to figs. 1–3, which show some typical results taken

Fig. 1.

Fig. 2.
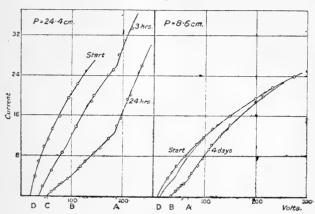
in the manner described. In its initially pure state the gas gives an ionic current for very low voltages, and (in those cases where the readings are completed before the conditions change appreciably) the curve is quite smooth over a large

range of voltage. From this it is to be inferred that the carriers in the gas are all electrons, moving so freely that very few become permanently attached to hydrogen molecules. This state of things does not last long. During the first few hours the electrons diminish in number and

Fig. 3.

freedom, while the appearance of heavier ions of definite mobility is marked by changes in slope of the curve occurring at definite voltages. Fig. 1 shows a typical case at a pressure of 68 cm. The initial curve has a slight upward curvature, showing that some material ions are already formed, the smoothness of the curve indicating that the electrons forming these ions traverse part of the journey between the plates free, and the remainder attached to a molecule. For an abrupt change of slope in the curve it is requisite that the ions be in definite allignment at one plate when beginning their journey, and that they preserve their character throughout the journey. The second curve was taken after an interval of three hours. It shows a diminished electronic freedom (D), while the two ions C and B appear at about 100 and 230 volts respectively. The readings have not been extended far enough in this case to indicate the normal ion A, but, judging from other curves, it is likely that there would only be a small proportion present at this stage. After one day the ion A is shown largely predominant, B and C being indicated in smaller proportions, while D is wholly absent. If at this stage the collected impurities from the charcoal bulb are admitted to the

chamber, the mobility of A is much reduced (20 per cent., say), and at most only traces of lighter ions can be detected.

The values deduced from a large number of curves are here tabulated. Notation, as in previous paper :—

Distance between plates, $d =$ (1) 6·4 cm.

(2) 4·2 cm.

E = reading of voltmeter at critical voltage = amplitude $/\sqrt{2}$.

$n = 50$ alternations per sec.   Mean temp. $= 15°$ C.

TABLE I.

Positive Ion.

Press. cm.	E. volts.	$u.$ cm./sec.	$1/u.$	$P \times u.$
2·1	36	127	·0079	266
5·0	31	63·1	·0158	316
9·8	57	34·3	·0292	337
14·8	81	24·1	·0415	356
18·5	236	19·4	·0516	359
24·6	303	15·1	·0663	371
29·4	354	12·9	·0774	380
35·0	416	11·0	·0910	385
39·3	197	9·88	·1012	388
44·9	517	8·85	·1130	397
52·7	255	7·66	·1307	404
60·0	290	6·74	·1486	404
63·2	303	6·45	·1552	406
70·9	337	5·80	·1725	415
77·5	365	5·36	·1867	415

TABLE II.

Negative Ion A.

Press. cm.	E. volts.	$u.$ cm./sec.	$1/u.$	Press. cm.	E. volts.	$u.$ cm./sec.	$1/u.$
8·6	65	70·4	·0142	58·3	440	10·4	·0961
13·8	107	42·8	·0234	*58·4	413	11·1	·0902
18·4	144	31·7	·0315	60·6	462	9·9	·1010
23·9	182	25·1	·0399	63·5	480	9·5	·1050
26·3	200	22·8	·0438	*67·7	468	9·8	·1021
35·7	270	16·9	·0591	68·4	512	8·9	·1120
37·2	282	16·2	·0617	71·3	229	8·5	·1171
*45·8	330	13·8	·0722	*76·8	506	9·1	·1104
*50·6	365	12·5	·0798	77·5	251	7·8	·1285
51·5	388	11·8	·0848				

Mean value $P \times u = 604·7$

Table III.

Negative Ion B.

Press. cm.	E. volts.	u. cm./sec.	1/u.	Press. cm.	E. volts.	u. cm./sec.	1/u.
8·6	33	139	·0072	*56·0	195	23·4	·0426
18·4	70	65·3	·0153	58·3	220	20·8	·0481
23·5	37	52·1	·0192	60·6	230	19·9	·0503
24·4	94	48·7	·0206	63·5	244	18·7	·0534
26·3	97	47·1	·0212	*68·4	255	18·0	·0557
36·3	138	33·1	·0302	*71·1	232	19·7	·0507
39·3	63	31·0	·0323	*75·5	230	19·9	·0503
41·3	159	28·8	·0348	76·4	137	15·7	·0536
*49·8	176	26·0	·0385	77·5	126	15·1	·0645
51·3	194	23·6	·0424				

Mean value $P \times u = 1206$

* The asterisks in the Tables indicate those values which are plotted but were excluded from the calculation of the mean value of Pu.

Table IV.

Negative Ion C.

Press. cm.	E. volts.	u. cm./sec.	1/u.	$P \times u$
56·0	85	53·8	·0186	3010
67·7	100	45·7	·0218	3105
75·4	113	40·5	·0247	3054

Mean value $P \times u = 3084$

Discussion.

In fig. 4 the reciprocal of the mobility is shown plotted against the pressure for all the ions. The values from the tables are marked by darker rings. For the sake of comparison, the values of Chattock † and of Franck ‡ and Pohl are marked by crosses with initials (atmospheric pressure). The differences in my values indicate that purifying the gas has the effect of making the positive ion less mobile and the negative ion more mobile. A similar result is noted by Wellisch § for the ions in air when the drying is very thoroughly carried out.

† Chattock, Phil. Mag. 1899, ser. 5, vol. xlviii. p. 401, and 1901, ser. 6, vol. i. p. 79.
‡ Franck & Pohl, *Verh. d. Deut. Phys. Ges.* 1907, p. 69.
§ Wellisch, Amer. Journ. Sc. May 1915.
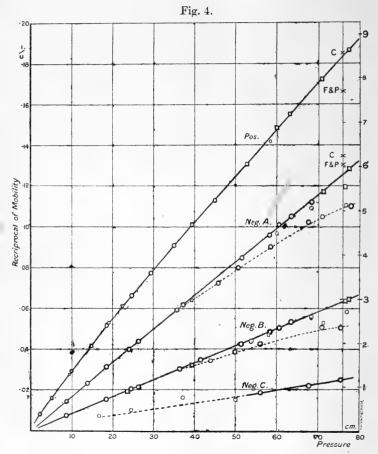
There was no consistent evidence of more than one kind of positive ion. The values indicate a departure from the law $Pu = $ const., especially at lower pressures, when the mobility is smaller than would be predicted.

Both the negative ions A and B follow this law very closely, the constant in the one case being just half that in the other. At pressures higher than half an atmosphere some readings give a mobility higher than is indicated by the formula, the dotted curves showing approximately the limits

Fig. 4.

within which the values lie. This would be the case if the limit were exceeded at which the proportionality of velocity to field breaks down, *i. e.* the velocity impressed on the ion being sufficient to cause it to break up and become lighter.

To test this, the distance d was lessened so that the voltages concerned in calculating the mobility were smaller. These values are distinguished in fig. 4 by squares instead of circles. The same tendency to higher values was noticeable, though perhaps not so marked. It is concluded that in some specimens of gas at higher pressures there is a genuine tendency for the normal value of the mobility of both A and B to be exceeded. At atmospheric pressure the velocity can be taken as proportional to the field up to *at least* a velocity of 700 cm./sec.

With regard to ion C * the results are not so definite or complete. In order that the interpretation of a curve shall be above question the ions D and B should be shown on either side, and in order that the measurement shall be accurate there must be a large number of the ions concerned present. These conditions are rarely fulfilled together. Also with the lighter ions the various portions of the curve are more crowded together, and a single inaccurate point may obscure its meaning. Three reliable values are recorded in Table IV., and several others are plotted. This represents the best that could be done with the present disposition of the apparatus. There is not sufficient evidence to decide whether or not more than one kind of ion is included in this group. The required changes are being made in the experimental arrangements in order that a further investigation may be made in this direction.

The more mobile ions are always the first to disappear as the contamination grows, and they are much more sensitive to impurities at higher pressures than at lower. The relative proportions of the various ions can be roughly estimated from the change in slope of the curve at the point of inflexion concerned. Thus in two cases where the gas had stood for a day the ratios of B/A were :—·2 at 76 cm. and 2·0 at 24 cm., showing clearly the greater stability of ion B at the lower pressure in spite of the fact that the contamination of the gas must be much larger in this case. Assuming that the effective impurity is the oxygen content of the air which leaks into the apparatus, rough measurements give :—

Press.,   9 cm.,   2·0 per cent. oxygen,   ratio B/A = 3·4
        18   ·6   ,,   ·6
        37   > ·2   ,,   ·2

---

   * *Note.*—It should here be remarked that the values given in the first paper as referring to ion C are spurious. The ions really present at the time of measurement were A and B with a small number of a lighter ion, the latter just sufficing to obscure the measurement for B. The curves were not traced out in sufficient detail to make this distinction clear.

At higher pressures the contamination is largely that from the walls of the apparatus. These facts are in the direction that would be expected, since at lower pressures there are fewer encounters per second between the molecules of the gas and therefore less opportunity for the ionic aggregates to increase their size. In other words, there is greater stability of light ions at lower pressures. For similar reasons the foreign molecules present in the hydrogen have greater influence at higher pressures. Since the electrons do not readily attach themselves to hydrogen molecules, the first step in the formation of most of the hydrogen ions is, no doubt, the capturing of an electron by a foreign molecule having the necessary affinity. And the greater the frequency of collision the greater the chance of the electrons being quickly taken captive.

The formula for the mobility of an ion as derived from the theory of gases is given by Townsend * as :

$$u = \cdot 815 \frac{\mathrm{X}et}{m\mathrm{V}},$$

t/V being the mean time between collisions. For a hydrogen molecule with a single electronic charge $e/m = 4 \cdot 78 \times 10^3$, $\mathrm{X} = 10^8$. The values † for t/V vary between $1 \cdot 052 \times 10^{-10}$ (N. T. P.) and $1 \cdot 186 \times 10^{-10}$ (15° C., Kundt and Warburg). The former value gives $u = 41 \cdot 0$ cm./sec., which corresponds very nearly to the measurements for ion C ($u = 40 \cdot 6$ at 76 cm.). The second value gives $u = 46 \cdot 2$, and this bears a close integral relationship to the measurements for the other ions. This is made plain in the accompanying Table, in which the theoretical mobilities for various molecular aggregates are shown, based on the assumption that the time between collisions is the same for aggregates as for single molecules, and the measured values placed beside them.

Ion.	Neg. C.	Neg. B.	Neg. A.	Pos.	
Experimental values u ...	40·6	15·9	7·9	5·4	⎫
Theoretical values u	46·2	15·4	7·7	5·1	⎬ 76 cm. press.
No. of mols. per electronic charge	1	3	6	9	⎭ and 15° C.

We conclude that the ions neg. C, neg. B, neg. A, and

* Townsend, 'Electricity in Gases,' 1915, p. 84.
† See Meyer, 'Theory of Gases,' p. 192.

positive are composed of aggregates whose simplest elements contain 1, 3, 6, and 9 molecules of hydrogen, respectively, per electronic charge. These integers are marked out as a scale in fig. 4, along the ordinate at one atmosphere, comparing theoretical values of u with actual.

These experiments explain clearly the results recorded by other workers on the subject, using methods which failed to distinguish between the different kinds of negative ions. Lattey and Tizard *, working at low pressures, remark on the need to use freshly prepared gas to obtain the high mobilities they record. They state that inconsistent results were obtained from hydrogen after it had stood for some time in the apparatus, which was, no doubt, due to the variable proportions in which ions A and B appeared. Also the large rise in mobility as the voltage increased was no doubt due—at least in part—to the failure to distinguish between ions of various mobilities. Chattock and Tyndall †, working at atmospheric pressure, found an exceptionally high mobility in pure hydrogen, and record quantitative measurements of the effect of the addition of small proportions of oxygen.

Summary.

Measurements are recorded of the mobilities of the positive ion and three different negative ions in hydrogen over a range of pressures between 8 cm. and 76 cm.

The results for two of the negative ions are expressed by the equations $Pu = 604 \cdot 7$ and $Pu = 1206$ respectively. The work for the third and lightest ion is not yet so complete.

Theoretical considerations indicate that the three negative ions are built up from elements containing one, three, and six molecules of hydrogen per electronic charge respectively, and the element in the positive ion has nine molecules per electronic charge.

Imperial College of Science and Technology.

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* Lattey and Tizard, Proc. Roy. Soc. 1912, p. 349.

† Chattock and Tyndall, Phil. Mag. 1910, ser. 6, vol. xix. p. 449.

XXXIX. *Strength of the Thin-plate Beam, held at its Ends and subject to a uniformly distributed Load (Special Case). By* B. C. Laws, *B.Sc., A.R.C.Sc.**

IN steel floating structures, as *e. g.* floating docks and ships, the shell plating supported at and rivetted to the frames or girders of the vessel is subject to hydrostatic pressure ; and, if we consider a section of the plate in a direction perpendicular to the frames, forms a case partaking of the nature of a beam continuous over its supports and encastré—subject to a uniformly distributed load.

The plating undergoes or tends to undergo distortion, and its appearance between consecutive frames is somewhat as indicated—but exaggerated for clearness—in fig. 1. In this

Fig. 1.

Plate Beam With a Uniformly Distributed Load w Per Square Inch.

figure r and r_1 denote the lines of rivets connecting the plate to the frames F, F_1, which latter are assumed to form rigid supports. The plating is deflected outwards between r and s, and r_1 and s_1 ; and inwards between the edges of the supports s and s_1, retaining the normal condition tangenital to the supports at r and r_1, where it is obviously subject to a pull or tensile force. It is the unknown value of this force which increases the difficulty of the problem.

In determining the thickness to be assigned to the plating, it is customary to consider the problem as a simple encastré beam of span something intermediate to ss_1 and rr_1. The assumption is erroneous, and the only explanation for it is that by its means the work of calculation is thereby very much reduced, while the results obtained are considered to be sufficiently near the truth for practical purposes.

From the mathematical standpoint, the problem should be approached as it is actually found to exist. The solution, by a direct process of rigorous mathematics, leads to complications due to the unknown conditions—of slope, force,

* Communicated by the Author.

&c.—existent at the ends of the beam. It may, however, be determined indirectly in a fairly simple manner by the aid of nothing more than the differential equation of the second order, and the object of this thesis is to indicate the method of attack.
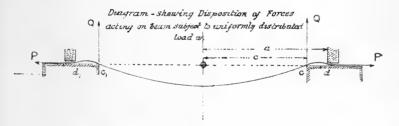
Consider a strip of plate, of unit width and thickness t, constituting a beam of length $rr_1 = 2a$, and subject to a uniformly distributed load w per unit length due to a head of water h.

Take the axis of X at the mid-surface of the plate, *i. e.*, in a plane distant $t/2$ from the supporting surfaces, o—the centre of the unsupported span—as origin, and the axis of Y downwards.

The appearance of the beam is shown diagrammatically in fig. 2.

Fig. 2.

acting on beam subject to uniformly distributed load w

The solution is obtained by dividing the problem into two parts, viz. :—

First. Assume the beam, under the action of a uniformly distributed load w per unit length (Q being removed), subject to a horizontal pull P and retaining its horizontality at the ends d and d_1 (fig. 3).

Fig. 3.
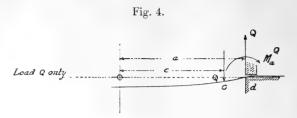
Second. Take the beam under the action of a concentrated

load Q only at c and c_1 with no pull at the ends and free to slide horizontally (fig. 4).

Fig. 4.

Load Q only

Obtain the deflexion at c (or c_1) in each case and impose the condition that these deflexions cancel each other—by reversing the direction of Q in fig. 4; we then have the beam as it actually is, and as indicated in fig. 2. The solution is given below :—

First. Consider w only (fig. 3) :—

$$-\mathrm{E}\cdot\mathrm{I}\frac{d^2y}{dx^2} = -\mathrm{M}_a^w - \mathrm{P}\cdot y + \frac{w(a^2 - x^2)}{2} \quad . \quad . \quad (1)$$

Put $\mathrm{P} = m^2\mathrm{E}\cdot\mathrm{I}$ and let θ be the inclination at any point of the curve, then $\frac{dy}{dx} = \tan\theta = \theta$, since θ must be small.

$$\frac{d^2y}{dx^2} = \frac{d\theta}{dx} = \frac{\mathrm{M}_a^w}{\mathrm{E}\cdot\mathrm{I}} + m^2y - \frac{w(a^2 - x^2)}{2\mathrm{E}\cdot\mathrm{I}}.$$

And $\qquad \dfrac{d^2\theta}{dx^2} = m^2\dfrac{dy}{dx} + \dfrac{w\cdot x}{\mathrm{E}\cdot\mathrm{I}} = m^2\theta + \dfrac{w\cdot x}{\mathrm{E}\cdot\mathrm{I}}.$

The solution of this equation is :—

$$\theta = \mathrm{A}\cdot e_0^{mx} + \mathrm{B}\cdot e_0^{-mx} - \frac{w\cdot x}{m^2\mathrm{E}\cdot\mathrm{I}},$$

and

$$-\mathrm{E}\cdot\mathrm{I}\frac{d\theta}{dx} = -\mathrm{E}\cdot\mathrm{I}\frac{d^2y}{dx^2} = -m\cdot\mathrm{E}\cdot\mathrm{I}(\mathrm{A}\cdot e_0^{mx} - \mathrm{B}\cdot e_0^{-mx}) + \frac{w}{m^2},$$

where e_0 is the base of the natural or Naperian logarithms.

When $x = a$, $\dfrac{dy}{dx} = \theta = 0$. $\therefore \mathrm{A}\cdot e_0^{ma} + \mathrm{B}e_0^{-ma} - \dfrac{w\cdot a}{m^2\mathrm{E}\cdot\mathrm{I}} = 0.$

When $x = 0$, $\dfrac{dy}{dx} = \theta = 0$. $\therefore A + B = 0$, or $A = -B$,

$$i.\,e.,\ \ A = -B = \frac{w\,.\,a}{m^2 E\,.\,I\,(e_0^{m.a} - e_0^{-m.a})}$$

$$\therefore -E\,.\,I\frac{d^2y}{dx^2} = -\frac{w}{m^2}\left\{\frac{m\,.\,a(e_0^{m.x} + e_0^{-m.x})}{e_0^{m.a} - e_0^{-m.a}} - 1\right\}$$

is the equation for bending-moment at any point of the beam.

When

$$x = a,\ \ -E\,.\,I\frac{d^2y}{dx^2} = M_a^w = -\frac{w}{m^2}\left\{\frac{m\,.\,a(e_0^{m.a} + e_0^{-m.a})}{e_0^{m.a} - e_0^{-m.a}} - 1\right\},$$

$$x = 0,\ \ -E\,.\,I\frac{d^2y}{dx^2} = M_0^w = -\frac{w}{m^2}\left\{\frac{2a\,.\,m}{e_0^{m.n} - e_0^{-m.a}} - 1\right\},$$

$$x = c,\ \ -E\,.\,I\frac{d^2y}{dx^2} = M_c^w = -\frac{w}{m^2}\left\{\frac{m\,.\,a(e_0^{m.c} + e_0^{-m.c})}{e_0^{m.a} - e_0^{-m.a}} - 1\right\}.$$

Now taking equation (1) we have :—

When $x = 0$, $M_0^w = -M_a^w - m^2 E\,.\,I\,.\,y_0^w + \dfrac{w\,.\,a^2}{2}$,

where $y_0^w = $ deflexion at o.

Combining this with the values for M_0^w and M_a^w we have:—

$$m^2 E\,.\,I\,.\,y_0^w = -\frac{w\,.\,a}{m}\left\{\frac{e_0^{m.a} + e_0^{-m.a} - 2}{e_0^{m.a} - e_0^{-m.a}}\right\} + \frac{w\,.\,a^2}{2}.$$

Similarly, if y_c^w be the deflexion at c,

$$m^2 E\,.\,I\,.\,y_c^w = -\frac{w\,.\,a}{m}\left\{\frac{(e_0^{m.a} + e_0^{-m.a}) - (e_0^{m.c} + e_0^{-m.c})}{e_0^{m.a} - e_0^{-m.a}}\right\} + \frac{w(a^2 - c^2)}{2}.$$

Second. Consider Q only (fig. 4).

There are two divisions of this problem : (a) For values of x ranging from 0 to c, and (b) for values of x ranging from c to a.

(a) For the portion oc of the beam :—

$$-\mathrm{E} . \mathrm{I}\frac{d^2y}{dx^2} = -\mathrm{M}_a^{\mathrm{Q}} + \mathrm{Q}(a-c).$$

$$\therefore \frac{dy}{dx} = \frac{\mathrm{M}_a^{\mathrm{Q}} - \mathrm{Q}(a-c)}{\mathrm{E} . \mathrm{I}} . x.$$

There is no constant of integration, since when $x = 0$. $\frac{dy}{dx} = 0$.

At c we have

$$\frac{dy}{dx} = \frac{\mathrm{M}_a^{\mathrm{Q}} . c - \mathrm{Q}(a-c)c}{\mathrm{E} . \mathrm{I}}.$$

(b) For the portion cd of the beam :—

$$-\mathrm{E} . \mathrm{I}\frac{d^2y}{dx^2} = -\mathrm{M}_a^{\mathrm{Q}} + \mathrm{Q}(a-x).$$

$$\therefore \frac{dy}{dx} = \frac{\mathrm{M}_a^{\mathrm{Q}} - \mathrm{Q} . a}{\mathrm{E} . \mathrm{I}} . x + \frac{\mathrm{Q} . x^2}{2\mathrm{E} . \mathrm{I}} + k,$$

where k is a constant.

When $x = a$, $\frac{dy}{dx} = 0$, and $k = -\frac{\mathrm{M}_a^{\mathrm{Q}} . a}{\mathrm{E} . \mathrm{I}} + \frac{\mathrm{Q} . a^2}{2\mathrm{E} . \mathrm{I}}.$

$$\therefore \frac{dy}{dx} = -\frac{\mathrm{M}_a^{\mathrm{Q}}(a-x)}{\mathrm{E} . \mathrm{I}} + \frac{\mathrm{Q}(a-x)^2}{2\mathrm{E} . \mathrm{I}}$$

$$= -\frac{\mathrm{M}_a^{\mathrm{Q}}(a-c)}{\mathrm{E} . \mathrm{I}} + \frac{\mathrm{Q}(a-c)^2}{2\mathrm{E} . \mathrm{I}} \therefore \text{at } c.$$

Equating the two values for $\frac{dy}{dx}$ at c, we have

$$\mathrm{M}_a^{\mathrm{Q}} = \frac{\mathrm{Q}(a^2 - c^2)}{2a}.$$

When $x = a$, $-\mathrm{E} . \mathrm{I}\frac{d^2y}{dx^2} = \mathrm{M}_a^{\mathrm{Q}} = -\frac{\mathrm{Q}(a^2 - c^2)}{2a}.$

When $x = 0$, $-\mathrm{E} . \mathrm{I}\frac{d^2y}{dx^2} = \mathrm{M}_0^{\mathrm{Q}} = -\mathrm{M}_a^{\mathrm{Q}} + \mathrm{Q}(a-c) = \frac{\mathrm{Q}(a-c)^2}{2a}.$

When $x = c$, $-\mathrm{E} . \mathrm{I}\frac{d^2y}{dx^2} = \mathrm{M}_c^{\mathrm{Q}} = \mathrm{M}_0^{\mathrm{Q}} = \frac{\mathrm{Q}(a-c)^2}{2a}.$

Again, referring to the portion cd :—

$$\frac{dy}{dx} = -\frac{M_a^Q(a-x)}{E \cdot I} + \frac{Q(a-x)^2}{2E \cdot I}.$$

$$\therefore y = -\frac{M_a^Q\left(ax - \frac{x^2}{2}\right)}{E \cdot I} + \frac{Q}{2E \cdot I}\left(a^2x - ax^2 + \frac{x^3}{3}\right) + C_1.$$

Now when $x = a$, $y = 0$.

$$\therefore C_1 = \frac{M_a^Q}{E \cdot I} \cdot \frac{a^2}{2} - \frac{Q}{2E \cdot I} \cdot \frac{a^3}{3}.$$

$$\therefore y = \frac{M_a^Q(a-x)^2}{2E \cdot I} - \frac{Q(a-x)^3}{6E \cdot I}$$

$$= \frac{Q(a-x)^2}{2E \cdot I}\left\{\frac{a^2-c^2}{2a} - \frac{a-x}{3}\right\},$$

and deflexion at $c = y_c^Q = \frac{Q(a-c)^3(a+3c)}{12aE \cdot I}.$

Also referring to the portion oc :—

$$\frac{dy}{dx} = \frac{M_a^Q - Q(a-c)}{E \cdot I}\,x,$$

$$\therefore y = \frac{M_a^Q - Q(a-c)}{E \cdot I} \cdot \frac{x^2}{2} + C_{11}.$$

Now when $x = c$,

$$y = y_c^Q = \frac{M_a^Q - Q(a-c)}{E \cdot I} \cdot \frac{c^2}{2} + C_{11} = \frac{Q(a-c)^3(a+3c)}{12aE \cdot I}.$$

$$\therefore y = \frac{Q(a-c)^2(a+2c)}{12E \cdot I} - \frac{Q(a-c)^2}{4aE \cdot I} \cdot x^2,$$

and deflexion at $o = y_0^Q = \frac{Q(a-c)^2(a+2c)}{12E \cdot I}.$

Now, in the general case fig. 2, c is level with d.

Therefore, putting $y_c^w = y_c^Q$ we get :—

$$\frac{Q(a-c)^3(a+3c)}{12a} = \frac{-w \cdot a}{m^3}\left\{\frac{(e_0^{m.a} + e_0^{-m.a}) - (e_0^{m.c} + e_0^{-m.c})}{e_0^{m.a} - e_0^{-m.a}}\right\} + \frac{w(a^2-c^2)}{2m^2},$$

an equation from which Q may be obtained when m is known.

The resultant bending-moments at o, c, and d, are :—
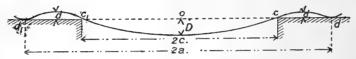
At o: $M_0^w - M_0^Q = -\dfrac{w}{m^2}\left\{ \dfrac{2a \cdot m}{e_0^{m.a} - e_0^{-m.a}} - 1 \right\} - \dfrac{Q(a-c)^2}{2a}.$

At c: $M_c^w - M_c^Q = -\dfrac{w}{m^2}\left\{ \dfrac{a \cdot m(e_0^{m.c} + e_0^{-m.c})}{e_0^{m.a} - e_0^{-m.a}} - 1 \right\} - \dfrac{Q(a-c)^2}{2a}.$

At d: $M_a^w - M_a^Q = -\dfrac{w}{m^2}\left\{ \dfrac{a \cdot m(e_0^{m.a} + e_0^{-m.a})}{e_0^{m.a} - e_0^{-m.a}} - 1 \right\} + \dfrac{Q(a^2 - c^2)}{2a}$

It will be found that the resultant bending-moment at c is the greatest, and must be used for calculating the stress in the material of the plate due to bending.

Fig. 5.

Now consider the diagram fig. 5, we have :—

Stress due to $P = \dfrac{m^2 t^2}{12} \cdot E$,

and elongation of the plate (beam) $= 2a \times \dfrac{m^2 t^2}{12} = \dfrac{m^2 t^2 a}{6}$.

Length of the curve $cc_1 = S = 2c + \dfrac{4D^2}{3c}$.

　　　,,　　　　,,　　　dc or $d_1 c_1 = s = (a-c) + \dfrac{8d^2}{3(a-c)}$.

Therefore elongation of the beam $= S + 2s - 2a$,

$$= \dfrac{4D^2}{3c} + \dfrac{16d^2}{3(a-c)} = \dfrac{m^2 t^2 a}{6},$$

or　　　　　　$D^2 + \dfrac{c}{a-c} \cdot 4d^2 = \dfrac{m^2 t^2 a \cdot c}{8}$,

an equation from which to determine t when D and d are known.

Now

$$D = y_0^w - y_0^Q = \dfrac{1}{E \cdot I}\left\{ -\dfrac{w \cdot a}{m^3}\left(\dfrac{e_0^{m.a} + e_0^{-m.a} - 2}{e_0^{m.a} - e_0^{-m.a}} \right) \right.$$
$$\left. + \dfrac{w \cdot a^2}{2m^2} - \dfrac{Q(a-c)^2(a+2c)}{12} \right\}.$$

And d may be taken—without appreciable error—as the deflexion at the point $x = \dfrac{a+c}{2}$; therefore, by considering the deflexion over the portion cd of the beam we have :—

$$d = \frac{w \cdot a}{m^3 \mathrm{E} \cdot \mathrm{I}} \left\{ \frac{e_0^{\frac{m(a+c)}{2}} + e_0^{\frac{-m(a+c)}{2}} - \left(e_0^{m.a} + e_0^{-m.a}\right)}{e_0^{m.a} - e_0^{-m.a}} \right\}$$

$$+ \frac{w(3a+c)(a-c)}{8m^2 \mathrm{E} \cdot \mathrm{I}} - \frac{\mathrm{Q}(a-c)^3(2a+3c)}{48a\mathrm{E} \cdot \mathrm{I}}.$$

It is noteworthy that the magnitude of d, being relatively very small, is only of theoretical significance, and, in the application of the above principles to practical problems, d may be neglected in comparison with D.

Summarising, the equations to be used in the calculation for strength of the beam are :—

(I.) To find Q from :—

$$\frac{\mathrm{Q}(a-c)^3(a+3c)}{12a} = -\frac{w \cdot a}{m^3} \left\{ \frac{\left(e_0^{m.a} + e_0^{-m.a}\right) - \left(e_0^{m.c} + e_0^{-m.c}\right)}{e_0^{m.a} - e_0^{-m.a}} \right\} + \frac{w(a^2-c^2)}{2m^2}.$$

(II.) To find t from :—

$$\frac{m^2 t^2 a \cdot c}{8} = \mathrm{D}^2 \qquad \text{or} \quad \mathrm{D} = mt\sqrt{\frac{a \cdot c}{8}},$$

where

$$\mathrm{D} = \frac{1}{\mathrm{E} \cdot \mathrm{I}} \left\{ -\frac{w \cdot a}{m^3} \left(\frac{e_0^{m.a} + e_0^{-m.a} - 2}{e_0^{m.a} - e_0^{-m.a}}\right) + \frac{w \cdot a^2}{2m^2} - \frac{\mathrm{Q}(a-c)^2(a+2c)}{12} \right\}.$$

(III.) To find the bending-moment from :—
Bending-moment at c

$$= -\frac{w}{m^2} \left\{ \frac{m \cdot a\left(e_0^{m.c} + e_0^{-m.c}\right)}{e_0^{m.a} - e_0^{-m.a}} - 1 \right\} - \frac{\mathrm{Q}(a-c)^2}{2a}.$$

In any specific case we have in (I.) and (II.) three equations from which to determine four unknown quantities Q, m, D, t.

If we assume a value of m then Q, D, and t may be determined, thence the bending-moment from (III.), and, finally, the stresses due to bending and stretching.

As an example take the case where :—

$a = 11$ inches, $c = 10$ inches.

$w = \cdot 007$ ton per inch run (equal to 36 ft. head of fresh water).
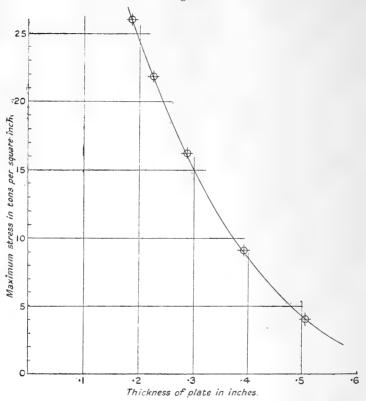
Assume for the purpose of our calculation $E = 13,500$ tons, and take $m = \cdot 1$.

From (I.) we get $Q = \cdot 385$.

From (II.) we get by the aid of (I.) :—

$$D = \frac{2 \cdot 813}{E \cdot I} = \frac{2 \cdot 813}{1125t^3} = t\sqrt{\frac{11}{80}}; \quad t^2 = \cdot 0821 \text{ and } t = \cdot 287 \text{ in.}$$

Fig. 6.

Maximum stress in tons per square inch.

Thickness of plate in inches.

From (III.) we get :—

Bending-moment at $c = \cdot 2071$.

Therefore :—

Stress intensity due to stretching $= \dfrac{P}{\text{sec}^l. \text{ area}} = \dfrac{m^2 E \cdot I}{t} = \cdot 924$ tons/in.²

,,   ,,   ,, bending $= \dfrac{\cdot 2071 \times 6}{t^2} = 15 \cdot 216$ tons/in.²

Or   Maximum tensile stress $= 16 \cdot 14$ tons/in.²

,, compressive ,, $= 14 \cdot 29$ tons/in.²

Similarly, by giving to m other values, we may determine corresponding stresses and plate thicknesses, from which data to construct a curve of "stress with relation to plate thickness," as shown in diagram fig. 6.

If we have previously decided upon the stress to be allowed in the material, we are able by the aid of this curve to determine the necessary thickness of plate required.

Thus for a stress of 10 tons per square inch (corresponding to a factor of safety of about 3 with mild steel) the thickness of plate required would be ·376 inch.

XL. *The Electrical and Magnetic Properties of Pure Iron in relation to the Crystal Size.* By F. C. THOMPSON, *M.Met., B.Sc., Demonstrator in Metallurgy in the University of Sheffield* [*].

DURING late years very considerable attention has been paid to the crystalline boundaries in metals, and the theory has been advanced, and received considerable support, that the metal at the crystal junctions is amorphous, corresponding in many respects to the liquid metal in a drastically undercooled condition. The mechanical effects resulting from such a structure are now fairly well known. The electrical and magnetic properties have not yet, however, received full examination from this point of view.

So long ago as 1902, Professor W. M. Hicks [†], commenting on the high permeability of iron alloyed with aluminium, pointed out that the elements aluminium, silicon, and phosphorus, which increased the permeability of iron, were the elements [‡] which had been shown by Arnold to increase the crystalline size of that metal. "It is probable, therefore, that the increase of permeability due to these substances is a secondary effect due to the size of the crystals." This idea would imply that the magneto-motive force required to send the magnetic flux through the body of the crystal itself is less than that necessary to send it across the glassy material at the crystal boundaries.

In an investigation on the relationship of the elastic limit of a metal to the size of the crystals [§], some electrical and

magnetic measurements were made on samples of very pure iron in which, as a result of appropriate heat-treatment, the size of the crystals varied to a marked extent, the material remaining otherwise unchanged. Iron was the metal chosen, since a greater variation of grain-size can be induced in it than is the case with most other metals. An ingot weighing 28 lb. was cast from a specially pure Swedish bar-iron, melted by the coke-crucible process. Before casting it 0·04 per cent. of aluminium was added to render the metal sound and free from blow-holes. The iron gave the following analysis :—

Carbon......................	0·049	per cent.
Silicon.....................	0·04	,,
Manganese	0 03	,,
Sulphur	0·02	,,
Phosphorus..............	0·016	,,

A trace only of aluminium remained in the ingot, whence the iron percentage by difference was 99·87 per cent. It is therefore one of the purest, if not the purest, ingot of iron ever made by this process. The specific resistance and the magnetic properties were determined in the following five conditions, in each of which the number of crystals per cm. length was carefully determined microscopically :—

(1) As received from the rolls.

(2) Normalized, *i. e.* re-heated to 900° C. in a muffle and cooled in air.

(3) Re-heated to 900° C. and cooled in a muffle during twelve hours.

(4) Re-heated to 900° C, maintained at this temperature for fifteen hours, and cooled in the furnace over another forty hours.

(5) Re-heated to 900° C., quenched in cold water, and tempered at 650° C. (This temperature was chosen since it is well above that—520° C.—at which iron deformed by cold work loses its strain[*]. Quenching strains which might conceivably vitiate the results are thus removed. Also the small percentage of carbon present will practically revert to the condition in which it is present in the other samples.)

By these treatments the number of crystals per cm. was varied from 690 in the quenched and tempered sample to about 10 in the drastically annealed one. In the latter case, however, some considerable irregularity in the crystal size— which though not readily explicable, is probably dependent

[*] Goerens, Journ. Iron & Steel Instit. Carnegie, vol. iii. (1911).

on the crystallization which occurs at the critical temperature Ac_3—rendered it unsuitable for the purpose of directly correlating the crystal size with the magnetic and electrical properties. The five specimens were cut consecutively from a single length of the rolled bar, between the two ends of which no difference of chemical composition could be detected. After treatment each of the small bars was turned down from the original diameter of one inch to a centimetre. Absolute freedom from alterations in composition due to surface decarburization was thus ensured.

(a) *Electrical Resistance.*

During the passage of an electric current through a normal metal the opposed resistance may be considered to be the sum of two factors, one for the actual crystalline material, the second depending on the resistance of the amorphous metal at the crystal boundaries. This amorphous metal, which, as already mentioned, is of the nature of an undercooled liquid, may be expected to possess a higher resistance than the crystals themselves, since a substance at its melting-point possesses a higher conductivity in the solid crystalline condition than in a liquid.

The thickness of the amorphous films is exceedingly small, probably of the order 10^{-5} cm.* Thus the length of the crystalline metal to be traversed by the current is essentially unaltered, whatever be the number of crystals per unit length. That part of the observed resistance due to the crystals themselves will, therefore, be a constant. On the other hand, however, the resistance of the boundaries will be proportional to the number of these regions of decreased conductivity which have to be traversed.

Thus, if

   ρ_1 is the observed specific resistance,
   ρ_2 is the specific resistance of the crystalline portion,
   n the number of crystals per cm., and
   R the boundary resistance for each grain,

then $$\rho_1 = \rho_2 + n\mathrm{R}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In order to check this relationship experimentally, bars 20 cm. long and 1 cm. in diameter were turned from each of the heat-treated samples. The specific resistance of each was determined by comparing the fall of potential over a definite length (15 cm.) with that in a standard low resistance through which the same current was flowing. The determinations were carried out at 16° to 17° C. In Table I. the

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* Thompson, Trans. Faraday Soc. i. (1915).

results are collected, together with those calculated by means
of equation (1). In every case an increase in the crystal
size is accompanied by a corresponding decrease of the
specific resistance. To about 1 per cent., which is quite as
near as the mean crystal size can be determined micro-
scopically, the relationship given above is found to hold
good.

TABLE I.

Specific Resistances of Pure Iron.

Treatment.	No. of Crystals per cm.	Specific Resistance in microhms per c.c.		
		Observed.	Calculated.	Difference.
As received	426	7·563	7·564	− ·001
Normalized	343	7·513	7·422	+ ·091
Annealed	276	7·251	7·307	− ·056
Drastically annealed	?	7·152	......	......
Quenched and tempered...	690	7·986	8·019	− ·033

The values experimentally obtained render it possible to
calculate the true specific resistance of the crystalline material
free from junctions, and substituting the mean values thus
found in equation (1), the specific resistance of any sample
of pure iron becomes

$$\rho = 6 \cdot 83 + 1 \cdot 72 n \times 10^{-3} \text{ microhm per c.cm.} \quad . \quad (2)$$

The value 6·83, the only rational one to adopt for the
constant for pure iron, is a value much less than that usually
adopted. In view of this result, no determination of the
specific resistance of any metal is complete which does not
give the crystal size and also sufficient data for the calcu-
lation of ρ_2. The wide divergence of the specific resistances
(7·15 to 7·99) seems to explain the great variation in the
values obtained for such "constants" by different investi-
gators, even when pure materials have been employed. The
variation observed in the case of iron is probably greater
than in that of most other metals, for instance copper, since
in these latter cases the crystalline structure is always coarse
compared with the normal crystallization of iron. Hence
the factor n is subject to smaller variations, and different
determinations show less discordance. One case in which

equation (1) is extended to metallic alloys is worthy of brief consideration here. Such alloys as consist entirely of a single solid solution should obey the rule equally with pure metals. It was found, however, in the course of an investigation on the effect of annealing on the electrical resistance of the copper-zinc-nickel alloys which belong to this class, that in many cases with a high nickel content the size of a crystal exercised no appreciable influence on the resistance. The values for an alloy containing 61·2 per cent. of copper, 9·81 per cent. zinc, and 28·6 per cent. nickel (*a*) with the very fine structure obtained immediately that re-crystallization had been induced, and (*b*) after subsequent prolonged annealing at 696° C. to coarsen the size of the crystals, were found to be 41·2 and 41·0 michroms per c.c. respectively. An explanation of this lack of dependence of the conductivity on the crystal size in these alloys, however, is not difficult, and the validity of the relationship (1) is not called in question. There is now little doubt that in solid solutions such as this alloy an internal strain of considerable magnitude must be assumed, which will re-act on the electrical conductivity, lowering it until, in certain cases, the conductivity of the crystalline and of the amorphous parts is practically the same.

Returning to the values of the specific resistance of iron, that obtained for the sample as received from the rolls (7·56) is in excellent agreement with the value (7·6) arrived at by Benedicks [*] by extrapolation of his results on the specific resistance of steels in the same condition. It is evident, however, that his equation for the specific resistance of steels

$$\rho = 7\cdot6 + 26\cdot8\,\Sigma C,$$

where ΣC is the sum of the carbon and the equivalents in carbon of the other elements present in solution, can only be be an approximation to the truth, since heat-treatment, *e. g.* annealing which varies the grain-size of the material without any chemical change, would result in a change of specific resistance.

An observation made during the present work on pure iron would seem to throw light on the conductivity of carbon steels. The drastically annealed sample of iron showed the curious irregularity already referred to. About nine-tenths of the mass consisted of crystals so coarse as to be readily

* Benedicks, 'Thesis for Doctorate,' Upsala, 1904.

visible to the naked eye after etching. The rest was composed of very much finer grains. The conductivity in this case was the greatest of any of the samples measured, but it was distinctly less than that corresponding to a specimen consisting of big crystals alone. The conductivity was, however, greater than would be expected from the relative proportions of the large and small crystals. These regions of fine and coarse crystallization are essentially so many circuits of higher and lower resistance, and it is to be expected that the current will pass preferentially through the coarser crystalline parts of lower resistance.

Now it has been shown by Benedicks [*] that the electrical resistance of steels containing less than 0·5 per cent. carbon varies with the carbon percentage in a different manner from that of steels with a higher carbon content. As a result of much careful work, it was concluded that about 0·27 per cent. carbon is present *in solution* in these latter steels giving a constituent "ferronite." It would seem, however, possible to explain the altered behaviour of the electrical properties of steel above and below 0·5 per cent. carbon in a simple manner. A low carbon steel consists of a matrix of iron crystals (ferrite) with isolated areas of pearlite in which the carbon present as Fe_3C is segregated. The electrical resistance of these latter areas is considerably greater than that of the ferrite (the specific resistance of pearlite being about 20 microhms per c.c.). Hence in such a steel the current will preferentially take a path through the ferrite. As the carbon content of the steel rises the pearlite increases at the expense of the ferrite, and at 0·45 per cent. the volumes of each are the same. Beyond this percentage, however, the relative order is reversed, and it is now the ferrite which occurs isolated in a background of pearlite. In this structure the continuous paths of the less resistant constituent are wanting; and it is not difficult to realize that the specific resistance now bears a somewhat different relationship to the carbon content from that which holds for those steels in which ferrite is the predominating constituent. Such an explanation removes the necessity for assuming the new constituent "ferronite." The fact, too, that, so far as the author has been able to determine, the pearlite areas in pure carbon steels free from silicon and manganese (which some of Benedicks' steels certainly were not) are directly proportional to the carbon content, is also

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[*] Benedicks, *loc. cit.*

opposed to any theory involving any large solubility of that element.

The mathematical expression here given for the relationship between the electrical resistance of a metal and the size of the component crystals is very similar to that given by Von Weimarn [*]. Regarding the question as being analogous with the electrical resistances of colloidal solutions, it was argued that the observed resistance of a metal is the sum of two values, the first of which is proportional to the volume of the sample, the second being dependent on the surface energy of the intercrystalline amorphous films. This latter value is obviously a function of the number of crystals per unit volume, while the first is a constant for each metal. The relationship, therefore, is almost identical with the author's, though it has been arrived at from a totally different point of view. Its validity is dependent on certain assumptions from which equation (1) is free, and no attempt was made to supply experimental evidence in support of the expression.

The speculation of Lord Rayleigh [†] concerning the influence of the Peltier effect on the electrical resistance of binary alloys offers a still more interesting subject for comparison. This was shown to result—in the case of immiscible components—in a back electromotive force (which simulates an added resistance) arising from the couples set up at the surfaces of contact of the two constituents. In a pure metal a similar result should flow from the presence of the amorphous films between the crystals. In the case of an alloy of fixed composition the increased resistance was shown to be independent of the number of the couples, *i. e.* of the number of crystals of each present. In the case under consideration, however, the conditions are somewhat different, since, as is probably the case, the films are of the same thickness with both big and little crystals. The *quantity* of the cement present in the latter case is thus increased, and considering the mass to be composed of disks of crystalline and amorphous material alternately, the amount of metal present in the latter state is n times the thickness of each film where n is the number of films, *i. e.* crystals per unit of length.

If e is the thermo-electric power of the couple formed by the components of the alloy, k and k' the thermal conductivity

* Von Weimarn, ' International Journal of Metallurgy,' iii. p. 65.
† Rayleigh, ' Nature,' liv. p. 154 (1896).

of the components, and p and q the fractional volume of each, then it was shown that the added resistance r

$$= \frac{273e^2}{\dfrac{k}{p} + \dfrac{k'}{q}},$$

a result which does not contain n. Now in a pure metal if p is the fraction of the volume composed of the crystalline material, and q that of the remaining amorphous metal, and if k and k' are of the same order of magnitude, then $\dfrac{k}{p}$ is negligible compared with $\dfrac{k'}{q}$, since the amount of the amorphous constituent is so small. Hence, approximately,

$$r = \frac{273e^2q}{k'}.$$

Since q is directly proportional to n, the increased resistance in a pure metal due to the intercrystalline films is also dependent on the number of crystals per cm. The total resistance of the metal is, therefore, expressed by an equation of exactly the same type as equation (1). Unfortunately, the data required for the comparison of this result with that (2) already determined experimentally are wanting, but the coincidence of the general type of the equation with that found experimentally is of the greatest interest, and affords further confirmation of the truth of the, at first sight, unlikely theory of the amorphous intercrystalline cement.

(B) *Magnetic Properties.*

The magnetic properties of the same samples of heat-treated iron were determined ballistically with the aid of Hicks' yoke. No correction has been applied for the reluctance of the latter, since relative values are sufficient for the present purpose of correlating crystalline size with magnetic properties. The results are summarized in Table II., and the hysteresis loops are reproduced in fig. 1.
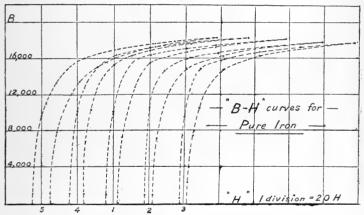
These results indicate that the maximum induction for a field of 95 gauss and the remanent magnetism are both, to all intents and purposes, independent of the size of the constituent crystals. They depend, therefore, apparently on the nature of the crystalline material rather than on the nature and number of the crystalline boundaries. The co-ercive force, however, increases regularly with the number

TABLE II.

Magnetic Properties of Pure Iron.

Treatment.	No. of Crystals per cm.	B(max.) for H =95.	B(rem.).	Hc.	Hysteresis loss.	Brinell Hardness.
As received	426	18250	10400	2·5	22900	86
Normalized	343	18550	10000	2·0	21400	83
Annealed	276	18200	10000	2·0	19200	74
Drastically annealed ...	?	18400	10000	4·0	24400	70
Quenched and tempered ...	690	18400	9600	5·0	34600	105

Fig. 1.

of crystals per unit length (the anomalous case of the drastically annealed sample will be considered later), and at the same time a corresponding increase in the hysteresis loss per cycle is found. In each case the relationship is an approximately linear one.

Along with the magnetic results the hardness values of the samples determined by Brinell's method are recorded. The load used was 500 kilograms, and the ball 10 mm. in diameter. The results are of interest in confirming the general impression that magnetic and mechanical hardness go side by side. With the exception, again, of the first sample, if the hysteresis loss per cycle is e and the Brinell hardness H, then

$$e = 30 \, H^{1 \cdot 5}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

When dealing with the electrical resistance of the drastically annealed sample, it was mentioned that the microstructure was remarkably uneven. The large grains, however, were the ones which seemed to exert most influence on the conductivity, which was the greatest of any of the specimens tested. The magnetic results, however, point in quite the opposite direction. With the exception of the quenched and tempered iron, the magnetic " hardness " of the drastically annealed sample was the greatest of all ; and the conclusion is inevitable that the minute crystals (despite their relatively small mass) had impressed their own properties on the whole sample.

The results are of practical importance in pointing to the possibility of producing by suitable annealing iron for transformers, &c., with far lower hysteresis losses than any yet obtained.

The constant values obtained for the maximum induction with varying crystal size hardly appears to be concordant with the view that the high permeability of iron alloyed with aluminium, silicon, or phosphorus is due to the large crystals which these elements induce. As an alternative suggestion, it may be noted that each of these three elements is used to remove the oxygen taken up by metals during melting. In the unalloyed iron it is probable that the oxygen is present partly as oxide in solid solution, a condition which in general decreases the permeability and increases the coercive force. The presence of silicon or aluminium would tend to eliminate the oxide from solution ; and it may be that to this fact the high permeability of the alloys of these elements with iron is to be referred.

XLI. *On the Hall Effect and Allied Phenomena.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

IN the October number of the Philosophical Magazine, in the paper by Mr. Livens on "The Electron Theory of the Hall Effect and Allied Phenomena," there are two points to which I would like to call attention. In discussing the reversal of sign which often occurs in the Hall effect, in the Nernst effect, in the Leduc effect, and in the von Ettingshausen effect, it is stated that, "It is, however, of importance to notice in this connexion that the signs of all the effects are found to be reversed if one of them is, or in other words, the effects always have the same relative direction. This observation is important as implying that the cause of the reversal is common to them all." An examination of the accompanying table, in which the direction of these effects has been indicated for a few metals, will show that the statement quoted above is inaccurate. There are some metals in which the reversal of signs occurs in accordance with the statement of Mr. Livens, but in the majority of cases it is otherwise.

Metal.	Hall Effect.	Nernst Effect.	Leduc Effect.	von Ettings- hausen Effect.
Bismuth............	−	−	−	+
Tellurium	+	−	+	+
Antimony	+	−	+	+
Cobalt	+	−	+	+
Silver	−	+	−	
Copper	−	+	−	
Silicon	{ −	−	...	+
	+	−		

In view of this discrepancy it seems impossible to account completely for this reversal of signs by a local magnetic field inside of the metal. In some cases the presence of this local magnetic field may afford a satisfactory explanation of the reversal of signs in the effects, but it does not afford a general explanation.

In discussing the influence of temperature on the Hall effect in the ferromagnetic metals, Mr. Livens states that, " In these cases as the temperature is increased the Hall effect coefficient increases, exactly parallel with the magnetic permeability, until the critical temperature is reached, when it decreases more rapidly to a value more akin to that found in the simpler metals. This would appear to be almost conclusive evidence of the appropriateness of the explanation of these irregularities suggested above." That there is a sudden decrease both in the Hall effect and in the permeability at the critical temperature cannot be questioned, but from this fact it is not to be inferred that the coefficient of the Hall effect and the permeability depend on the temperature in the same way. The Hall effect seems to be a more complicated function of the magnetic permeability than the statement quoted above seems to indicate.

Kundt has shown that the Hall electromotive force is proportional to the intensity of magnetization for a particular temperature. If E is the Hall electromotive force ; I, the intensity of magnetization ; k, the susceptibility ; H, the magnetizing force ; and A, a constant of proportionality,

$$E = A \times I = A \times k \times H.$$

For a given value of H the relation between the Hall electromotive force and the susceptibility is given by the equation

$$E/k = A \times \text{constant}.$$

If the Hall effect and the permeability increase parallel to each other, the ratio of the Hall electromotive force to the susceptibility should be independent of the temperature, that is A should be independent of the temperature. Experiments have shown that A is a function of the temperature and that it increases rather rapidly with the temperature. Hence the Hall effect and the permeability depend in different ways on the temperature, and the variation of the Hall effect with the temperature cannot be entirely accounted for by the variation of the permeability with the temperature.

<div align="right">Very truly yours,

ALPHEUS W. SMITH.</div>

Ohio State University,
    Columbus, O.

XLII. *On a Brief Proof of the Fundamental Formula for Testing the Goodness of Fit of Frequency Distributions, and on the Probable Error of "P." By* KARL PEARSON, *F.R.S.*[*]

1. IN a contribution to the 'Philosophical Magazine' in 1900 (vol. l. pp. 157–175) I gave the first proof of the fundamental formula for testing goodness of fit of a theoretical frequency curve or surface to observational data. The observational data were supposed to constitute a sample of definite size drawn from an indefinitely large population obeying the theoretical curve or surface of frequency. The problem proposed was : To measure the probability that a sample of the proposed size drawn from the indefinitely large theoretical population would present as great or greater divergence than the observed material does from the sampled population. Was, in fact, the observed population so improbable a sample of the theoretical distribution that it must be rejected as a sample by the prudent statistician ?

Let the theoretical population consist of M individuals falling into q classes with the frequencies $m_1, m_2, \ldots m_q$, all these classes being indefinitely large, but having finite ratios. Then, if a sample of size N give the classes $n_1, n_2, \ldots n_q$, the mean value of n_s in a long series of samples will be $\bar{n}_s = N m_s / M$, and the distribution of n_s will follow the binomial

$$\left\{ \frac{\bar{n}_s}{N} + \left(1 - \frac{\bar{n}_s}{N} \right) \right\}^N,$$

and accordingly, if no class be extremely small as compared with N, the distribution of any frequency like n_s will be approximately normal and the combined system of frequencies will follow the generalized Gaussian law

$$z = z_0 e^{-\frac{1}{2} \left\{ S_1 \left(\frac{\triangle_{ss}}{\triangle} \frac{x_s^2}{\sigma_s^2} \right) + 2 S_2 \left(\frac{\triangle_{ss'}}{\triangle} \frac{x_s x_{s'}}{\sigma_s \sigma_{s'}} \right) \right\}}, \quad . \quad . \quad . \quad \text{(i.)}$$

where

$$x_s = n_s - \bar{n}_s, \quad \sigma_s^2 = \bar{n}_s \left(1 - \frac{\bar{n}_s}{N} \right),$$

the squared standard deviation of the binomial, and the correlation of x_s and $x_{s'}$ or $r_{ss'}$, is given by

$$\sigma_s \sigma_{s'} r_{ss'} = - \frac{\bar{n}_s \bar{n}_{s'}}{N}.$$

Further, Δ stands for the determinant

$$\begin{vmatrix} 1 & r_{1,2} & r_{1,3} & \cdots & r_{1,q-1} \\ r_{2,1} & 1 & r_{2,3} & \cdots & r_{2,q-1} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ r_{q-1,1} & r_{q-1,2} & r_{q-1,3} & \cdots & 1 \end{vmatrix},$$

and $\Delta_{uu'}$ is the minor of the constituent $r_{uu'}$.

In the paper already referred to, I found the value of the exponential power by actually reducing the above determinant and its minors. I have since deduced other proofs, of which the present seems for lecture purposes the briefest.

In the expression (i.) above we must include only $q-1$ variate frequencies, as the qth frequency follows at once from these by the relation

$$N = n_1 + n_2 + \ldots + n_q,$$

the size of the sample N being fixed. Accordingly, S_1 is a sum for s from 1 to $q-1$, and S_2 a sum of products for all unlike pairs s and s' out of $1, 2, 3 \ldots s \ldots s' \ldots q-1$.

Now consider what happens when we fix the variates $x_1, x_2 \ldots x_{q-1}$, or all but x_s; then the equation to the frequency of x_s will be given by

$$z = z_0' e^{-\frac{1}{2}\frac{\Delta_{ss}}{\Delta}\frac{(x_s - h_s)^2}{\sigma_s^2}}$$

all the other terms being constant and falling into z_0'. $\Sigma_s^2 = \sigma_s^2 \Delta/\Delta_{ss}$ will give the standard deviation of this distribution. We can to determine Σ_s give the other x's their mean values, in which case we shall have samples of constant size $\bar{n}_s + \bar{n}_q$ to be taken out of the population. The standard deviation of such samples will then be given by

$$\Sigma_s^2 = (\bar{n}_s + \bar{n}_q)\frac{m_s}{m_s + m_q}\left(1 - \frac{m_s}{m_s + m_q}\right)$$

$$= (\bar{n}_s + \bar{n}_q)\frac{\bar{n}_s}{\bar{n}_s + \bar{n}_q}\left(1 - \frac{\bar{n}_s}{\bar{n}_s + \bar{n}_q}\right)$$

$$= \frac{\bar{n}_s \bar{n}_q}{\bar{n}_s + \bar{n}_q}.$$

Accordingly :

$$\frac{\Delta_{ss}}{\Delta \sigma_s^2} = \frac{1}{\Sigma_s^2} = \frac{1}{\bar{n}_s} + \frac{1}{\bar{n}_q}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(ii.)}$$

Thus the coefficient of x_s^2 in our exponential is determined.

Now consider the partial correlation coefficient of x_s and $x_{s'}$ for constant $x_1, x_2 \ldots x_{q-1}$ for all the $q-1$ variates except x_s and $x_{s'}$. We may put these constant variates zero, and it is clear that we have to find the correlation of x_s and $x_{s'}$ when we take samples of size $\bar{n}_s + \bar{n}_{s'} + \bar{n}_q$ from the m_s, $m_{s'}$, and m_q classes only.

But in this, if Σ'_s, $\Sigma'_{s'}$ be the standard deviations, we must have

$$\Sigma'^2_s = (\bar{n}_s + \bar{n}_{s'} + \bar{n}_q) \frac{m_s}{m_s + m_{s'} + m_q}\left(1 - \frac{m_s}{m_s + m_{s'} + m_q}\right)$$

$$= \bar{n}_s\left(1 - \frac{\bar{n}_s}{\bar{n}_s + \bar{n}_{s'} + \bar{n}_q}\right) = \frac{\bar{n}_s(\bar{n}_{s'} + \bar{n}_q)}{\bar{n}_s + \bar{n}_{s'} + \bar{n}_q}; \quad \cdot \quad \cdot \quad \cdot \quad \text{(iii.)}$$

and, similarly,

$$\Sigma'^2_{s'} = \frac{\bar{n}_{s'}(\bar{n}_s + \bar{n}_q)}{\bar{n}_s + \bar{n}_{s'} + \bar{n}_q}.$$

Further, if $\rho_{ss'}$ be the required correlation,

$$\rho_{ss'}\Sigma'_s\Sigma'_{s'} = -(\bar{n}_s + \bar{n}_{s'} + \bar{n}_q)\frac{m_s}{m_s + m_{s'} + m_q}\frac{m_{s'}}{m_s + m_{s'} + m_q}$$

$$= -\frac{\bar{n}_s\bar{n}_{s'}}{\bar{n}_s + \bar{n}_{s'} + n_q}.$$

Thus

$$\rho_{ss'} = -\frac{\sqrt{\bar{n}_s\bar{n}_{s'}}}{\sqrt{\bar{n}_s + \bar{n}_q}\sqrt{\bar{n}_{s'} + \bar{n}_q}}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(iv.)}$$

But by the general theory of multiple correlation,

$$\rho_{ss'} = -\frac{\Delta_{ss'}}{\sqrt{\Delta_{ss}\Delta_{s's'}}}$$

$$= -\frac{\Delta_{ss'}}{\sigma_s\sigma_{s'}\Delta}\bigg/\sqrt{\frac{\Delta_{ss}}{\sigma_s^2\Delta}\times\frac{\Delta_{s's'}}{\sigma_{s'}^2\Delta}},$$

or

$$\frac{\Delta_{ss'}}{\sigma_s\sigma_{s'}\Delta} = \frac{\sqrt{\bar{n}_s\bar{n}_{s'}}}{\sqrt{\bar{n}_s + \bar{n}_q}\sqrt{\bar{n}_{s'} + \bar{n}_q}}\sqrt{\left(\frac{1}{\bar{n}_s} + \frac{1}{\bar{n}_q}\right)\left(\frac{1}{\bar{n}_{s'}} + \frac{1}{\bar{n}_q}\right)},$$

using the values found for (ii.). Thus we deduce

$$\frac{\Delta_{ss'}}{\sigma_s\sigma_{s'}\Delta} = \frac{1}{\bar{n}_q}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(v.)}$$

Accordingly we have found the coefficient of the term $x_s x_{s'}$ in the power of the exponential, which may now be written

$$z = z_0 e^{-\frac{1}{2}\chi^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(vi.)}$$

where we have

$$\chi^2 = S_1\left(\frac{\Delta_{ss}}{\Delta}\frac{x_s^2}{\sigma_s^2}\right) + 2S_2\left(\frac{\Delta_{ss'}}{\Delta}\frac{x_s x_{s'}}{\sigma_s \sigma_{s'}}\right)$$

$$= S_1\left\{x_s^2\left(\frac{1}{\bar{n}_s}+\frac{1}{\bar{n}_q}\right)\right\} + 2S_2\left\{\frac{x_s x_s}{\bar{n}_q}\right\}$$

$$= S_1\left(\frac{x_s^2}{\bar{n}_s}\right) + \frac{1}{\bar{n}_q}(x_1+x_2+\ldots+x_{q-1})^2.$$

Now $S(n_s) = N, \quad S(\bar{n}_s) = N$;

and therefore

$$x_1+x_2+ \ldots +x_{q-1}+x_q = 0$$

and $(x_1+x_2+ \ldots +x_{q-1})^2 = x_q^2.$

Thus finally we have for χ^2

$$\chi^2 = S\left(\frac{x_s^2}{\bar{n}_s}\right),$$

where the summation is for all values of x_s from 1 to q.

There are, however, only $q-1$ independent variables, and accordingly the chance that a sample of N will occur with a value of the deviation-complex of magnitude χ^2 or greater is

$$P = \frac{\int_{\chi}^{\infty} \chi^{q-2} e^{-\frac{1}{2}\chi^2} d\chi}{\int_{0}^{+\infty} \chi^{q-2} e^{-\frac{1}{2}\chi^2} d\chi}.$$

This is the value of P calculated in the tables of the "goodness of fit," and accordingly all turns on the determination of

$$\chi^2 = S\left\{\frac{(n_s-\bar{n}_s)^2}{\bar{n}_s}\right\}.$$

2. *On the Probable Error of the Determination of Goodness of Fit.*

If $\chi^2 = S_1^q\left\{\frac{(n_s-\bar{n}_s)^2}{\bar{n}_s}\right\},$

then in a recent memoir * the probable error of χ^2 has been found, or rather σ_{χ^2}.

* Young and Pearson: *Biometrika*, vol. xi. part ii.

Now *

$$P_q = \frac{\int_{\chi}^{\infty} e^{-\frac{1}{2}\chi^2} \chi^{q-2} d\chi}{\int_0^{\infty} e^{-\frac{1}{2}\chi^2} \chi^{q-2} d\chi},$$

$$\delta P_q = \frac{-e^{-\frac{1}{2}\chi^2} \chi^{q-2} d\chi}{\int_0^{\infty} e^{-\frac{1}{2}\chi^2} \chi^{q-2} d\chi},$$

or

$$\sigma_{P_q} = \sigma_\chi \cdot \chi \cdot \frac{e^{-\frac{1}{2}\chi^2} \chi^{q-3}}{\int_0^{\infty} e^{-\frac{1}{2}\chi^2} \chi^{q-2} d\chi}$$

$$= \tfrac{1}{2}\sigma_{\chi^2} \times \psi_q(\chi),$$

where

$$\psi_q(\chi) = \frac{e^{-\frac{1}{2}\chi^2} \chi^{q-3}}{\int_0^{\infty} e^{-\frac{1}{2}\chi^2} \chi^{q-2} d\chi}.$$

Now suppose q is even: then

$$\int_0^{\infty} e^{-\frac{1}{2}\chi^2} \chi^{q-2} d\chi = (q-3)(q-5)\ldots 1 \times \int_0^{\infty} e^{-\frac{1}{2}\chi^2} d\chi.$$

Thus, since

$$\int_0^{\infty} e^{-\frac{1}{2}\chi^2} d\chi = \sqrt{\pi/2},$$

$$\psi_q(\chi) = \sqrt{\frac{2}{\pi}} e^{-\frac{1}{2}\chi^2} \frac{\chi^{q-3}}{1 \cdot 2 \cdot 3 \ldots q-3}$$

$$= P_q(\chi^2) - P_{q-2}(\chi^2) \;\dagger.$$

Next suppose q is odd : then

$$\int_0^{\infty} e^{-\frac{1}{2}\chi^2} \chi^{q-2} d\chi = (q-3)(q-5)\ldots 2 \int_0^{\infty} e^{-\frac{1}{2}\chi^2} \chi \, d\chi.$$

Thus, since

$$\int_0^{\infty} e^{-\frac{1}{2}\chi^2} \chi \, d\chi = 1,$$

$$\psi_q(\chi) = P_q(\chi^2) - P_{q-2}(\chi^2) \;\dagger,$$

the same value as before.

* Phil. Mag. *loc. cit.* p. 158, Eq. (iii.), remembering that $n = q-1$ =number of independent variables.

† Phil. Mag. *loc. cit.* p. 159, Equations (v.) and (vi.).

Hence generally,

$$\sigma_{P_q} = \tfrac{1}{2}\sigma_{\chi^2}(P_q(\chi^2) - P_{q-2}(\chi^2)).$$

The values of P for the value of χ^2 and for q and $q-2$ can be taken directly from the Tables for Goodness of Fit [*]. The value of σ_{χ^2} is given by

$$\sigma_{\chi^2} = \left\{ 2(q-1) + \frac{q}{H} + \frac{q(q-2)}{N} \right\}^{\frac{1}{2}},$$

where q = number of cells as before and H is the harmonic mean of their contents [†]. It is thus fairly easy to determine the standard deviation of P, and so ascertain whether the degree of " goodness of fit " is sufficiently stable to provide in any case an adequate measure of fit.

Illustration I.—We may illustrate the method on the data provided in the introduction to my ' Tables for Statisticians,' p. xxxii, for the goodness of fit of the cephalic index of 900 Bavarian crania to a Gaussian distribution. The following table gives the observed and Gaussian frequencies :—

Cephalic Index.	Observed.	Gaussian.
Under 75·5	9·5	12·4
75·5–76·5	12·5	12·7
76·5–77·5	17	22·1
77·5–78·5	37	35·3
78·5–79·5	55	51·9
79·5–80·5	71·5	70·1
80·5–81·5	82	87·0
81·5–82·5	116	99·4
82·5–83·5	98	104·2
83·5–84·5	107	100·5
84·5–85·5	82	89·1
85·5–86·5	74	72·6
86·5–87·5	58	54·3
87·5–88·5	34·5	37·4
88·5–89·5	19	23·7
89·5–90·5	10	13·8
90·5–91·5	8	7·4
Over 91·5	9	6·3

These 18 groups give $\chi^2 = 10\cdot27$, leading to P $= \cdot8909$.
The n's are, of course, given by the Gaussian column, and from this H can be calculated by aid of tables of reciprocals. Thus

$$S\left(\frac{q}{H}\right) = S\left(\frac{1}{n_s}\right) = \cdot786{,}272{,}53.$$

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[*] ' Tables for Statisticians,' p. 26.
[†] Young and Pearson, *loc. cit.*, where we must note that $\chi^2 = N\phi^2$.

Further,
$$2(q-1) = 34, \quad q(q-2)/N = \cdot 32.$$
Accordingly,
$$2(q-1) + \frac{q}{H} + \frac{q(q-2)}{N} = 35 \cdot 106,272,53,$$
and
$$\sigma_{\chi^2} = \{35 \cdot 106,272,53\}^{\frac{1}{2}} = 5 \cdot 9256.$$

Since χ^2 is only $10 \cdot 27$, this indicates that the material might quite easily be a sample from the Gaussian given.

Now
$$P_q(\chi^2) = \cdot 8909 \quad \text{and} \quad P_{q-2}(\chi^2) = \cdot 8016,$$
thus
$$\tfrac{1}{2}\{P_q(\chi^2) - P_{q-2}(\chi^2)\} = \cdot 04465.$$

This leads to
$$\sigma_P = 5 \cdot 9256 \times \cdot 04465 = \cdot 2646,$$
and probable error of $P = \cdot 1785$.

The result may therefore be given as
$$P = \cdot 89 \pm \cdot 18.$$

It will be seen that the test of goodness of fit is subject to a larger probable error than has hitherto been realized. It will not in this case affect our judgment, for P is so large that the large probable error will not reduce it to a really small probability, but it indicates that, especially in considering relative goodness of fit, we must proceed with caution in this matter.

Illustration II.—I will consider the application of the present theory to fourfold tables, and take as examples two tables cited on p. xxxiv of my 'Tables for Statisticians' for characters of fruit and flower in *Datura* and for Eye-colour in father and son. The tables are :—

(i.) *Datura.*   (ii.) Eye-colour in Father and Son.

		Colour of Flower.		
		Violet.	White.	Totals.
Fruit.	Prickly ...	47	21	68
	Smooth ...	12	3	15
	Totals...	59	24	83

		Father.		
		Light.	Not-Light.	Totals.
Son.	Light	471	148	619
	Not-Light.	151	230	381
	Totals...	622	378	1000

The "theoretical" tables in this case are those with independent variates, *i. e.*,

(i.)

48·3373	19·6627	68
10·6627	4·3373	15
59	24	83

(ii.)

385·018	233·982	619
236·982	144·018	381
622	378	1000

The χ^2 are

$$\text{(i.) } \chi^2 = ·7080, \qquad \text{(ii.) } \chi^2 = 133·3265.$$

The reciprocals of $\bar{n}$'s are to be found from the "theoretical" tables. But if we have a fourfold table:

a	b	$a+b$
c	d	$c+d$
$a+c$	$b+d$	N

a little consideration shows that

$$\mathrm{S}\left(\frac{1}{n_s}\right) = \frac{\mathrm{N}^3}{(a+b)(c+d)(a+c)(b+d)},$$

if the condition of zero contingency be satisfied.
Hence we find

$$\frac{q}{\mathrm{H}} = \mathrm{S}\left(\frac{1}{\bar{n}_s}\right) = ·395,8866 \text{ for (i.),}$$
$$= ·018,0344 \text{ for (ii.) ;}$$
$$2(q-1) = 6 \text{ for both;}$$
$$\frac{q(q-2)}{\mathrm{N}} = ·096,3855 \text{ for (i.),}$$
$$= ·008 \text{ for (ii.).}$$

Accordingly,

$$\sigma_{\chi^2} = \{6·492,2721\}^{\frac{1}{2}} = 2·5480 \text{ for (i.),}$$
$$= \{6·026,0344\}^{\frac{1}{2}} = 2·4548 \text{ for (ii.).}$$

It is clear that σ_{χ^2} depends chiefly on the term $2(q-1)=6$, and will be generally for fourfold tables very near

$$\sqrt{6} = 2·4495.$$

Thus we have

$$\chi^2 = ·7080 \pm 1·7186 \text{ for (i.),}$$
$$\chi^2 = 133·3265 \pm 1·6557 \text{ for (ii.);}$$

and record that the total frequency in (i.), or 83, was inadequate to determine χ^2, while that in (ii.) was adequate to give χ^2 with about 3 per cent. possible error.

We now consider the standard deviation of P. This for a fourfold table is

$$\sigma_P = \tfrac{1}{2}\sigma_{\chi^2} \cdot \{P_4(\chi^2) - P_2(\chi^2)\}.$$

The value of $P_2(\chi^2)$ is not tabled in the Tables for Goodness of Fit, for the simple reason that it is provided in the Tables of the Probability Integral *. In fact, for $n = 4$ †,

$$P = \sqrt{\frac{2}{\pi}} \int_{\chi}^{\infty} e^{-\frac{1}{2}\chi^2} d\chi + \sqrt{\frac{2}{\pi}} \chi e^{-\frac{1}{2}\chi^2}.$$

$$\therefore \delta P = \sqrt{\frac{2}{\pi}} \left(-e^{-\frac{1}{2}\chi^2} - \chi^2 e^{-\frac{1}{2}\chi^2} + e^{-\frac{1}{2}\chi^2} \right) d\chi$$

$$= -\sqrt{\frac{2}{\pi}} \chi e^{-\frac{1}{2}\chi^2} (\chi \, d\chi);$$

or $\qquad \sigma_P = \dfrac{1}{2}\sqrt{\dfrac{2}{\pi}} \chi e^{-\frac{1}{2}\chi^2} \sigma_{\chi^2}$

$$= \frac{1}{2}\sigma_{\chi^2} \left(P_4(\chi) - \sqrt{\frac{2}{\pi}} \int_{\chi}^{\infty} e^{-\frac{1}{2}\chi^2} d\chi \right),$$

or $\quad P_2(\chi) = \sqrt{\dfrac{2}{\pi}} \displaystyle\int_{\chi}^{\infty} e^{-\frac{1}{2}\chi^2} d\chi = 2 \times \tfrac{1}{2}(1-\alpha) = 2 \times \{1 - \tfrac{1}{2}(1+\alpha)\},$

where $\tfrac{1}{2}(1+\alpha)$ is the probability integral ‡.

Now $\chi^2 = \cdot 7080$ and therefore $\chi = \cdot 84143$ for (i.), and $\chi^2 = 133 \cdot 3265$ and therefore $\chi = 11 \cdot 54671$ for (ii.).

We can find $P_2(\chi)$ for (i.) at once by interpolating between $\cdot 84$ and $\cdot 85$ in the tables for the probability integral. There results $\tfrac{1}{2}(1+\alpha) = \cdot 799945$, and therefore $\tfrac{1}{2}(1-\alpha) = \cdot 200055$ and $P_2(\chi) = \cdot 40011$ for (i.), but $P_4(\chi) = \cdot 8713$. Hence

$$\sigma_P = \frac{1}{2} \, 2 \cdot 5480 (\cdot 8713 - \cdot 4001) = \cdot 6003.$$

Thus we deduce $\cdot 4049$ for the probable error of P in (i.).

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* This fact has, of course, been known since the first "goodness of fit" table was calculated, but was overlooked by certain American writers. I therefore gave a proof in a joint paper by Dr. Heron and myself, *Biometrika*, vol. ix. p. 312.

† 'Tables for Statisticians,' p. xxxi.

‡ *Loc. cit.* p. 2.

In the Eye-colour case the determination of P_2 (11·54671) must be a little less accurate, for the ordinary tables do not go to such high values of the argument. Interpolating between the values of $-\log F$ for 11 and 12 in Table IV. of the 'Tables for Statisticians,' we find

$$-\log F(11\cdot54671) = 30\cdot46966,$$

or
$$\log F = \overline{31}\cdot53034.$$

Hence
$$\tfrac{1}{2}(1-\alpha) = 3\cdot3911/10^{31}$$

and
$$P_2(\chi) = 6\cdot7822/10^{31} = \cdot007/10^{28}.$$

But [*]
$$P_4(\chi) = 1\cdot035/10^{28};$$

thus
$$\sigma_P = \frac{1}{2}\,2\cdot4548(1\cdot035/10^{28} - \cdot007/10^{28})$$

$$= 1\cdot2618/10^{28}.$$

Thus the probable error of P is $\cdot851/10^{28}$.
The numerical results for the two cases are:

    (i.) $P = \cdot8713 \pm \cdot4049,$

    (ii.) $P = 1\cdot035/10^{28} \pm \cdot851/10^{28}.$

Now the whole range of P is from 0 to 1, and the probable error of P shows that within the limits of random variation P for the *Datura* table may be anything from 0 to 1. The data are accordingly absolutely inadequate for the purpose of indicating whether or no colour of flower and prickliness of fruit are associated. In the second case the probable error is such that P might really be zero, but it is not such that P could ever be replaced by anything but another indefinitely small probability. In other words, the data are amply sufficient to demonstrate that eye-colours in parent and child are definitely associated. On the other hand, the large value of the probable error of P, *relative to the size of* P *itself*, justifies a further emphasis of the caution given above to compare indefinitely small magnitudes of P of different orders with considerable reservation.

[*] 'Tables for Statisticians,' p. xxxv.

XLIII. *Long-range Alpha Particles from Thorium.* *By* Sir ERNEST RUTHERFORD, *F.R.S., and* A. B. WOOD, *M.Sc., Lecturer in Physics, University of Liverpool* *.

IN the course of an examination of a strong source of the active deposit of thorium by the scintillation method, one of us observed the presence of a small number of bright scintillations which were able to penetrate through a thickness of matter corresponding to 11·3 cm. of air at 760 mm. and 15° C. These scintillations were undoubtedly due to alpha particles and of greater velocity than any previously observed; for the swiftest alpha particles hitherto known, viz. those from thorium C, have a range in air of 8·6 cm. The number of these long-range alpha particles is only a small fraction of the total number emitted by the source. The actual number of long-range particles decreased exponentially with time, falling to half value in 10·6 hours— the normal period of decay of the active deposit of thorium. Owing to the pressure of other work, the experiments were kindly repeated and extended by Mr. A. B. Wood, who examined in detail the variation of the number of scintillations with thickness of matter traversed. There are still a number of points that require further examination, but as neither of the authors is likely to have time to continue the experiments in the near future, it has been thought desirable to give a brief account of the preliminary results.
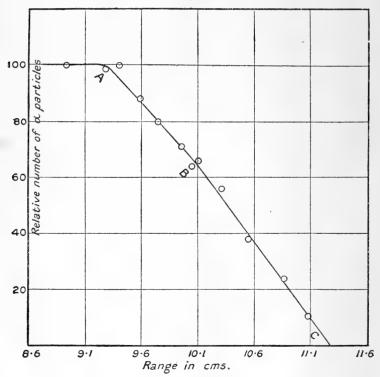
Experimental arrangements.

The end of a brass rod, 1 mm. in diameter, was exposed as negative electrode in a small vessel containing a strongly emanating preparation, either of radio-thorium or meso-thorium. By suitable adjustment of the electrodes, the active deposit was concentrated almost entirely on the end of the rod—a condition essential to the accurate determination of the ranges. After two days' exposure to the electric field, the wire was removed and placed end-on at 4 mm. distance from a small screen of zinc sulphide viewed with a low-power microscope. Care was taken that the axis of the microscope passed through the centre of the rod. The screen was permanently covered with a mica plate whose thickness corresponded to 8·6 cm. of air—the maximum range of the alpha particle from thorium C. All scintillations then observed were due to alpha particles which had passed through the mica plate and 4 mm. of air, *i. e.* a distance

* Communicated by the Authors.

corresponding to 9 cm. of air. With the most intense source available, about 20 scintillations per minute were counted on the microscope. The number fell off rapidly with increase of distance of the source, but an occasional α particle was still observed at a distance of 2 cm. from the source. In order to determine the variation of number of these particles with distance of matter traversed, thin screens of aluminium, each corresponding in thickness to 1·25 mm. of air, were successively interposed between the source and screen. It was found that the number of long-range particles remained constant between 8·6 and 9·3 cm. of air, but decreased in number from 9·3 cm., vanishing at 11·3 cm. The grouped average of all the observations in a large number of experiments is shown in fig. 1.

Fig. 1.
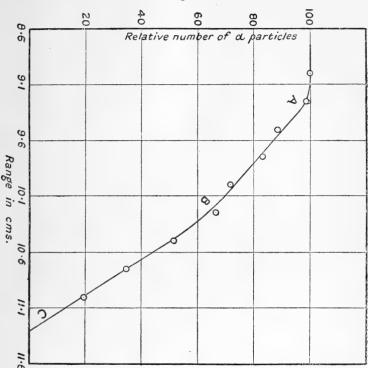
It is seen that the curve shows evidence of two fairly definite slopes AB, BC, as if there were two sets of alpha particles present of different ranges. This important point

was very carefully examined, and the results of a special series of observations are shown in fig. 2. It will be seen that there appears to be a fairly definite change in the slope when the number of scintillations is reduced to about two-thirds of the total.

Fig. 2.

It will be seen from the curves that the alpha particles start decreasing in number from about 2 cm. of the maximum range. The variation of number with distance is much slower than that to be expected for a single group of alpha particles of corresponding range. This is brought out in fig. 3, which shows the results obtained when the scintillation-distance curve in air was obtained for the two well-known groups of alpha particles emitted from thorium C of ranges 5·0 and 8·6 cm. respectively. In these cases, the scintillations fall off rapidly, beginning at about 1 cm. from the end of the corresponding range. The difference between the slopes of the scintillation-curve for the long-range alpha particles and those from thorium C cannot be explained by the oblique

path taken by some of the rays through the mica on account
of the nearness of the source and screen.   Calculations
showed that the influence of obliquity could only account for
a small fraction of the difference actually observed.

Fig. 3.

The results we have so far obtained certainly seem to
indicate either that (1) the long-range alpha particles are
expelled with variable velocities over a comparatively narrow
range, and in this respect differ markedly from alpha particles
from ordinary radioactive products which are known to be
expelled with identical velocity, or (2) that two homogeneous,
groups of alpha rays of characteristic ranges are present.   In
order to distinguish definitely between these two hypotheses,
it would be necessary to count many thousands of alpha
particles, but other evidence suggests that (2) is the more
probable explanation.

The slope AB ends at about a range 10·2 cm. and when
the number of alpha particles is reduced to about two-thirds

of the total. This suggests that two groups of homogeneous rays are present, one-third of maximum range 10·2 cm. and two-thirds of range 11·3 cm. The slope of the scintillation curve to be expected on this hypothesis agrees within the experimental error with the observed curve. This division of the alpha particles into two homogeneous groups may be compared with the two well-known groups of alpha particles emitted from thorium C, for it is known that one-third have a range 5·0 cm. and two-thirds a range 8·6 cm. This suggests that the new groups of alpha particles have their origin in thorium C, and that one-third of range 10·2 cm. accompany the alpha particles of range 5·0 cm., and the remainder of range 11·3 cm. accompany the alpha particles of range 8·6 cm. While it is very difficult to prove the correctness of such a deduction, the numerical agreement in the divisions of alpha particles of different ranges is certainly striking.

We have not so far examined experimentally whether the new alpha particles are expelled from the alpha ray product thorium C, but this seems very probable. To settle this point, it will be necessary to prepare a strong preparation of thorium C and to determine whether the period of transformation, measured by the new alpha particles, is in agreement with the accepted value for thorium C, viz. half value in 60 minutes.

Number of Long-range Alpha Particles.

Since the number of long-range particles decreases at the same rate as the alpha-ray activity of the active deposit of thorium, it is convenient to express their number as a fraction of the total number of alpha particles emitted per second from thorium C. For this purpose, the number of long-range particles per minute was measured with the source fixed at a known distance from the screen. The active deposit was then allowed to decay *in situ* for 32 hours. The absorbing screen was then removed and the number of alpha particles from thorium C measured at distances from 6 to 7 cm., so as to include only the longer range alpha particles (8·6 cm.) from thorium C. In this way it was found that the fraction of long-range alpha particles was 1/6700. Taking into consideration that the alpha particles of range 8·6 cm. from thorium C are two-thirds of the total, the fraction becomes 1/10000.

Preliminary observations by different methods gave a somewhat lower value, but the above number cannot be much in error. We thus see that the long-range alpha particles

are expelled in a very small proportion (1/10000) compared with the ordinary alpha particles. Unless a very intense source be employed, it will not be easy to detect the presence of the long-range alpha particles when the ordinary alpha particles are first absorbed by a layer of 8·6 cm. of air.

In the Bragg ionization curves from thorium C given by Marsden and Perkins *, a small residual activity is to be noticed beyond the distance 8·6 cm. which is relatively more marked than for the corresponding curve for radium C. This no doubt is to be ascribed to the effect of the very long-range alpha particles.

Discussion of Results.

It is now well established that thorium C is anomalous in breaking up in two distinct ways. One-third of the atoms are transformed with the emission of alpha particles of range 5·0 cm., and the remainder gives alpha particles of range 8·6 cm. These modes of transformation of thorium C have been examined in detail by Marsden and Darwin †, and an ingenious scheme of changes has been suggested to account for the facts observed. It is known that the products corresponding to thorium C in the radium and actinium series, viz. radium C and actinium C, also have two distinct modes of transformation. Fajans ‡ showed that 1/6000 of the atoms of radium C give rise to a new product of half period 1·38 minutes, which emits beta rays in its transformation. In a similar way actinium C has been found to emit two sets of alpha particles of range 5·4 and 6·4 cm. § This is ascribed to a double mode of transformation, 1·5/1000 of the atoms breaking up with the emission of alpha particles of range 6·4 cm.

Assuming that the new alpha particles of thorium can be divided into two homogeneous groups of range 10·2 and 11·3 cm., it is seen that thorium C must break up in four distinct ways with the expulsion of alpha particles of ranges 5·0, 8·6, 10·2, and 11·3 cm. at 15° C.

The possible modes of transformation of thorium C are thus more complicated than was at first supposed, and it is obvious that the suggestions given by Marsden and Darwin as to the modes of transformation of this substance can be

* Marsden & Perkins, Phil. Mag. xxvii. p. 691 (April 1914).
† Marsden & Darwin, Proc. Roy. Soc. A lxxxvii. p. 17 (1912); see also Marsden & Barratt, Proc. Phys. Soc. xxiv. 1, p. 50 (1911); Marsden & Wilson, Phil. Mag. xxvi. p. 354 (1913).
‡ Fajans, *Phys. Zeit.* xii. p. 369 (1911); xiii. p. 699 (1912).
§ Marsden & Perkins, Phil. Mag. xxvii. p. 694 (1914).

only a partial explanation. From the close analogy of the " C" products of radium, thorium, and actinium, it is probable that further examination will show an analogous complexity in the modes of breaking up of radium C and actinium C. The loss of energy in the form of expelled alpha particles is very different in the four modes of transformation of thorium C, and in consequence it does not seem likely that the resulting products can be the same in all cases. The differences in the energies emitted by the two branch products of thorium C formed a serious difficulty in the original explanation given by Marsden and Darwin of the two main modes of transformation of thorium C, and this difficulty is now further increased. A more detailed discussion on these interesting points will be reserved until further experimental information is available. The relation found by Geiger between the range of the expelled alpha particles and the life of the radioactive product, suggests that the average life of the atoms which expel the long-range alpha particles must be exceedingly short, and of the order of 10^{-13} and 10^{-16} sec. for the products emitting alpha particles of range 10·2 and 11·3 cm. respectively.

The following table gives the velocity of the four groups of alpha particles from thorium C, taking as the basis of calculation the measurements of Rutherford and Robinson that the velocity V of the alpha particles from radium C of range 6·94 cm. at 15° C. is $1·922 \times 10^9$ cm. per second, and assuming Geiger's relation $V^3 = kR$ where R is the range.

	Range at 15° C.	Ratio of velocities.	Calculated velocity.
Thorium C$_1$	4·95 cm.	1	$1·71 \times 10^9$ cm.
Thorium C$_2$	8·6 ,,	1·205	2·06 ,, ,,
New product (C$_3$)......	10·2 ,,	1·275	2·18 ,, ,,
New product (C$_4$)......	11·3 ,,	1·32	2·26 ,, ,,

Recently one of us [*] showed by direct measurement that the velocities in two main groups of alpha particles from thorium C were in good agreement with the calculated values if the range of the alpha particles from thorium C$_1$ is 4·95 cm. instead of 4·80 cm.—the value usually taken. From our measurements, there appears to be no doubt that the higher value is more correct.

[*] A. B. Wood, Phil. Mag. xxx. p. 702 (1915).

Summary.

Evidence is given that the active deposit of thorium emits a small number of alpha particles of greater velocity than any previously observed. These alpha particles are believed to have their origin in the transformation of thorium C, and appear to be divided into two homogeneous groups of maximum range 10·2 and 11·3 cm. The number of these alpha particles is about 1/10000 of the total number emitted from thorium C, two-thirds of the number having a range 11·3 cm.

The results indicate that the atoms of thorium C can break up in three and probably four distinct ways with the emission of four characteristic groups of alpha particles of ranges 5·0, 8·6, 10·2, and 11·3 cm.

University of Manchester,
    February 1916.

XLIV. *On Waves due to a Travelling Disturbance, with an application to Waves in Superposed Fluids. By* Horace Lamb, *F.R.S.*[*]

1. IN any case of wave-propagation in one dimension a distribution of impulse of amount $\cos kx$ per unit length gives rise to an oscillation of the type

$$\eta = \phi(k) \cos kx \, e^{i\sigma t}, \quad \cdots \quad (1)$$

where σ is a function of k determined by the theory of free waves. The effect of a concentrated unit impulse at the origin is accordingly given by a Fourier expression

$$\eta = \frac{1}{\pi} \int_0^\infty \phi(k) \cos kx \, e^{i\sigma t} dk$$

$$= \frac{1}{2\pi} \int_0^\infty \phi(k) e^{i(\sigma t - kx)} dk + \frac{1}{2\pi} \int_0^\infty \phi(k) e^{i(\sigma t + kx)} dk . \quad (2)$$

To avoid possible indeterminateness in the sequel we may introduce a factor $e^{-\mu t}$ to represent the effect of slight dissipative action. If it is required in order to make the integrals convergent, we may suppose μ to be a suitable function of k, but it will serve our purpose if we take μ to be constant, and in the end infinitesimal.

To find the wave-system due to a concentrated disturbing force of unit magnitude travelling with the velocity c in the direction of x-negative, we may take the origin at the instantaneous position of the disturbing influence. The result of an impulse δt delivered at an antecedent time t is

[*] Communicated by the Author.

given by (2), if we replace x by $ct-x$, and multiply by δt. Integrating from $t=0$ to $t=\infty$, we obtain

$$\eta = \frac{1}{2\pi}\int_0^\infty \left\{ \int_0^\infty \phi(k)e^{i\sigma t - ik(ct-x)}e^{-\mu t}dk + \int_0^\infty \phi(k)e^{i\sigma t + ik(ct-x)}e^{-\mu t}dk \right\} dt.$$
$$. \quad . \quad . \quad (3)$$

In the absence of the factor $e^{-\mu t}$ the result would in some cases be indeterminate, the physical reason being that we can superpose a system of free waves having the prescribed velocity c, if such are possible.

The integration with respect to t gives

$$\eta = \frac{1}{2\pi}\int_0^\infty \frac{\phi(k)e^{ikx}dk}{\mu - i(\sigma - kc)} + \frac{1}{2\pi}\int_0^\infty \frac{\phi(k)e^{ikx}dk}{\mu - i(\sigma + kc)} \quad . \quad (4)$$

The coefficient μ being supposed small, the most important part of the result will be due to values of k in the first integral which make

$$\sigma = kc, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

approximately, if such exist. Writing, then, $k = \kappa + k'$, where κ is a root of (5) and k' is assumed to be small, we have

$$\sigma - kc = \left(\frac{d\sigma}{dk} - c\right)k' = (\mathrm{U}-c)k', \quad . \quad . \quad (6)$$

nearly, where U is the group-velocity corresponding to the wave-velocity c. The important part of (4) is therefore

$$\eta = \frac{1}{2\pi}\phi(\kappa)e^{i\kappa x}\int_{-\infty}^\infty \frac{e^{ik'x}dk'}{\mu - i(\mathrm{U}-c)k'}, \quad . \quad . \quad (7)$$

since the extension of the range of integration to $k' = \pm\infty$ makes no serious difference.

The integral comes under a known form. If a be positive, we have

$$\int_{-\infty}^\infty \frac{e^{imx}dm}{a+im} = \left\{ \begin{array}{c} 2\pi e^{-ax}, \; [x>0] \\ 0 \quad ; \; [x<0] \end{array} \right\} \quad . \quad . \quad (8)$$

whilst

$$\int_{-\infty}^\infty \frac{e^{imx}dm}{a-im} = \left\{ \begin{array}{c} 0 \quad , \; [x>0] \\ 2\pi e^{ax} . \; [x<0] \end{array} \right\} \quad . \quad . \quad (9)$$

Hence if $\mathrm{U}<c$, we have

$$\eta = \frac{\phi(\kappa)e^{i\kappa x}}{c-\mathrm{U}}e^{-\mu x/(c-\mathrm{U})}, \text{ or } 0, \quad . \quad . \quad (10)$$

according as $x \gtrless 0$; whilst if $\mathrm{U}>c$,

$$\eta = 0, \text{ or } \frac{\phi(\kappa)e^{i\kappa x}}{\mathrm{U}-c}e^{\mu x/(\mathrm{U}-c)}, \quad . \quad . \quad . \quad (11)$$

in the respective cases.

2 D 2

Putting now $\mu = 0$, we have the simple expression

$$\eta = \frac{\phi(\kappa) e^{i\kappa x}}{|c - U|}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (12)$$

for the wave-train generated by the travelling disturbance. The train follows or precedes the disturbing agent according as $U \lessgtr c$. Examples of the two cases are furnished by gravity waves on water, and capillary waves, respectively.

If there is more than one value of k satisfying (5), there will, of course, be a term of the above type for each such value. This happens in the case of water-waves due to gravity and capillarity combined, and in the example treated more particularly below.

If the expansion of $\sigma - kc$ in powers of k' were continued the next term would be $\frac{1}{2} k'^2 dU/dk$, and it is therefore necessary for the validity of the above approximation that the ratio

$$\frac{1}{2} k' \frac{dU}{dk} \Big/ (U - c)$$

should be small even when $k'x$ is a moderate multiple of 2π. The ratio

$$\frac{dU}{dk} \Big/ (U - c) x$$

must therefore be small. Unless $U = c$ exactly, this condition is always fulfilled when x is sufficiently great. It may be added that the results (10) and (11) are accurate in the sense that they give correctly the leading term in the evaluation of (4) by Cauchy's method of residues.

2. If the value of k which satisfies $\sigma = kc$ also happens to make $U = c$, the procedure must be modified. We write, then,

$$\sigma - kc = \frac{1}{2} \frac{dU}{dk} k'^2 = \pm \frac{\mu}{2\beta^2} k'^2, \quad \cdot \quad \cdot \quad \cdot \quad (13)$$

say. Taking the case of the upper sign, we have

$$\eta = \frac{i\beta^2}{\pi\mu} \phi(\kappa) e^{i\kappa x} \int_{-\infty}^{\infty} \frac{e^{ik'x} dk'}{k'^2 + 2i\beta^2}. \quad \cdot \quad \cdot \quad \cdot \quad (14)$$

This can be evaluated by contour integration. The value of the integral is found to be

$$\frac{2\pi i \, e^{i(-1+i)\beta x}}{2(-1+i)\beta}, \quad \text{or} \quad \frac{2\pi i \, e^{i(1-i)\beta x}}{2(1-i)\beta},$$

according as x is positive or negative. Hence, for $x > 0$,

$$\eta = \frac{\phi(\kappa)}{\sqrt{(2\mu d\mathrm{U}/dk)}} e^{-\beta x} \cdot e^{i(\kappa - \beta)x + \frac{1}{4}i\pi}, \quad . \quad . \quad (15)$$

and, for $x < 0$,

$$\eta = -\frac{\phi(\kappa)}{\sqrt{(2\mu d\mathrm{U}/dk)}} e^{\beta x} \cdot e^{i(\kappa + \beta)x + \frac{1}{4}i\pi} . \quad . \quad . \quad (16)$$

The wave-system now extends on both sides the origin. For a moderate range of x we may put $\beta = 0$ in the exponentials; thus

$$\eta = \pm \frac{\phi(\kappa)}{\sqrt{(2\mu d\mathrm{U}/dk)}} e^{i(\kappa x + \frac{1}{4}\pi)}. \quad . \quad . \quad . \quad (17)$$

If $d\mathrm{U}/dk$ is negative we must take the lower sign in (13). The result is, with the simplification referred to,

$$\eta = \pm \frac{\phi(\kappa)}{\sqrt{(-2\mu d\mathrm{U}/dk)}} e^{i(\kappa x - \frac{1}{4}\pi)}. \quad . \quad . \quad . \quad (18)$$

Here, as in (17), the upper or lower sign is to be taken according as $x \gtrless 0$.

3. The formula (12) may be used to reproduce a number of known results. Thus, in the case of an impulsive pressure $\cos kx$ on the surface of deep water, the consequent surface-elevation is

$$\eta = -\frac{k}{\rho\sigma} \sin \sigma t \cos kx . \quad . \quad . \quad . \quad (19)$$

To conform to (1) we must put

$$\phi(k) = \frac{ik}{\rho\sigma}, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and take the real part. Hence, for the train of waves following a unit concentrated pressure, we find

$$\eta = -\frac{2}{\rho c^2} \sin \kappa x, \quad . \quad . \quad . \quad . \quad (21)$$

which is the known result. We have here made use of the relations $\sigma = \kappa c$, $\mathrm{U} = \frac{1}{2}c$.

Again, in the case of water of finite depth h, the result of a surface-impulse $\cos kx$ is easily found to be

$$\eta = -\frac{k}{\rho\sigma} \tanh kh \sin \sigma t \cos kx. \quad . \quad . \quad (22)$$

We therefore write

$$\phi(k) = \frac{ik}{\rho\sigma} \tanh kh. \quad . \quad . \quad . \quad (23)$$

In this case we have

$$\sigma^2 = gk \tanh kh, \quad \cdots \quad (24)$$

and

$$c - U = \frac{1}{2} c \left(1 - \frac{2kh}{\sinh 2kh} \right) \quad \cdots \quad (25)$$

Hence for the effect of a travelling disturbance, we find

$$\eta = -\frac{2}{\rho c^2} \cdot \frac{\sinh^2 \kappa h}{\sinh \kappa h \cosh \kappa h - \kappa h} \sin \kappa x. \quad \cdots \quad (26)$$

This, again, is in accordance with a known result *.

The critical case of $U = c$ occurs when we have water-waves subject to gravity and capillarity combined, if the velocity c of the travelling disturbance is equal to Kelvin's minimum wave-velocity. Since

$$\sigma^2 = gk + T'k^3, \quad \cdots \quad (27)$$

where T' is the ratio of the surface-tension to the density, we find, in the critical case,

$$\frac{dU}{dk} = \frac{c}{2\kappa}. \quad \cdots \quad (28)$$

Taking the value of $\phi(k)$ from (20), and substituting in (17), we have

$$\eta = \mp \frac{\kappa^{\frac{1}{2}}}{\mu^{\frac{1}{2}} \rho c^{\frac{3}{2}}} \sin \left(\kappa x + \frac{1}{4} \pi \right). \quad \cdots \quad (29)\dagger$$

The critical values of κ and c are given by

$$\kappa = \sqrt{(g/T')}, \quad c^2 = 2\sqrt{(gT')} \quad \cdots \quad (30)$$

4. The formula (12) supplies all that is essential for calculations of wave-resistance. If we denote the potential energy of the waves, per unit length of the axis of x, by

$$\frac{1}{2} C\eta^2,$$

where C is a coefficient depending on the nature of the medium, the mean energy, both potential and kinetic, in the wave-train will be

$$E = \frac{1}{2} C \frac{|\phi(\kappa)|^2}{(c - U)^2}, \quad \cdots \quad (31)$$

absolute value being indicated in case $\phi(\kappa)$ is imaginary.

Supposing, for definiteness, that $U < c$, let a fixed point

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* Lamb, 'Hydrodynamics,' 4th ed., Art. 245.

† *Cf.* Rayleigh, Proc. Lond. Math. Soc. (1) vol. xv. p. 75 (1883); 'Scientific Papers,' vol. ii. p. 264.

be taken in the rear of the disturbing body. Owing to the
extension of the wave-train the space in front of this point
gains energy to the amount cE per unit time, whilst the
energy transmitted at the fixed point is UE, by the dynamical
property of group-velocity. The difference is equal to the work
done by the force (R) which generates the waves. Hence

$$R = \frac{c-U}{c} E = \frac{1}{2} C \frac{|\phi(\kappa)|^2}{c(c-U)} \quad . \quad . \quad . \quad (32)$$

If $U > c$, the fixed point must be taken in advance of the
disturbing body, and $c - U$ is replaced by $U - c$.

5. The application to waves in superposed fluids has an
interest, owing to its bearing on the phenomenon of "dead-
water" [*].

Suppose we have a stratum of depth h and density ρ
resting on a liquid of greater density ρ' whose depth is prac-
tically infinite. The problem of free waves in this case was
solved long ago by Stokes [†]. If the origin be taken in the
upper surface, with the axis of y drawn vertically upwards,
we may write

$$\phi = (A \cosh ky + B \sinh ky) \cos kx \cos \sigma t, \quad . \quad (33)$$

$$\phi' = C e^{ky} \cos kx \cos \sigma t, \quad . \quad . \quad . \quad . \quad (34)$$

the two formulæ relating to the upper and lower fluids
respectively.

If η, η' denote vertical displacements of a particle, we
have

$$\frac{d\eta}{dt} = -\frac{\partial \phi}{\partial y}, \quad \frac{d\eta'}{dt} = -\frac{\partial \phi'}{\partial y}, \quad . \quad . \quad (35)$$

whence

$$\eta = -\frac{k}{\sigma}(A \sinh ky + B \cosh ky) \cos kx \sin \sigma t, \quad . \quad (36)$$

$$\eta' = -\frac{k}{\sigma} C e^{ky} \cos kx \sin \sigma t \quad . \quad . \quad . \quad (37)$$

The variation of pressure about a particle is given by

$$p = \rho \left(\frac{\partial \phi}{\partial t} - g\eta \right), \quad p' = \rho' \left(\frac{\partial \phi'}{\partial t} - g\eta' \right) \quad . \quad (38)$$

In order that the pressure at the upper surface may be
constant we must have, therefore,

$$\frac{\sigma^2}{gk} A - B = 0. \quad . \quad . \quad . \quad . \quad (39)$$

* Ekman, *l. c. infra.*
† "On the Theory of Oscillatory Waves," Camb. Trans. vol. viii.
(1847); Math. and Phys. Papers, vol. i. p. 212.

The continuity of pressure at the interface between the two liquids requires

$$\left(\frac{\sigma^2}{gk}\cosh kh + \sinh kh\right)\rho A - \left(\frac{\sigma^2}{gk}\sinh kh + \cosh kh\right)\rho B$$
$$= \left(\frac{\sigma^2}{gk} - 1\right)e^{-kh}\rho' C. \quad . \quad . \quad (40)$$

The condition that the vertical displacement at the interface must be the same for the two liquids gives

$$A \sinh kh - B \cosh kh = -C e^{-kh} \quad . \quad . \quad . \quad (41)$$

This system of equations has two solutions, which it is convenient to distinguish by suffixes. In the first of these we have

$$\sigma_1^2 = gk, \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

as in the case of a single fluid, with

$$B_1 = C_1 = A. \quad . \quad . \quad . \quad . \quad . \quad (43)$$

In the second solution we have

$$\sigma_2^2 = \frac{gk(\rho' - \rho)\sinh kh}{\rho'\cosh kh + \rho\sinh kh}, \quad . \quad . \quad (44)$$

with

$$\frac{B_2}{A_2} = \frac{\sigma_2^2}{gk}, \quad \frac{C_2}{A_2} = -\frac{\rho e^{2kh}}{\rho' - \rho}\frac{\sigma_2^2}{gk}. \quad . \quad . \quad (45)$$

The wave-velocities corresponding to these two modes of oscillation are given by

$$c_1 = \frac{\sigma_1}{k}, \quad c_2 = \frac{\sigma_2}{k}. \quad . \quad . \quad . \quad . \quad (46)$$

As the wave-length $(2\pi/k)$ increases from 0 to ∞, c_2 increases from 0 to an upper limit c_0, given by

$$c_0^2 = \left(1 - \frac{\rho}{\rho'}\right)gh. \quad . \quad . \quad . \quad . \quad (47)$$

If U_1, U_2 be the corresponding group-velocities, we have

$$c_1 - U_1 = \frac{1}{2}c_1, \quad . \quad . \quad . \quad . \quad . \quad (48)$$

$$c_2 - U_2 = \frac{1}{2}c_2\left\{1 - \frac{\rho'}{\rho'\cosh kh + \rho\sinh kh}\cdot\frac{kh}{\sinh kh}\right\}$$
$$= \frac{1}{2}c_2\left\{1 - \left(\frac{kh}{\sinh kh}\right)^2\frac{c_2^2}{c_0^2}\right\} \quad . \quad . \quad . \quad (49)$$

As the wave-length increases from 0 to ∞, U_2 increases from $\frac{1}{2}c_2$ to c_0.

From this point we may without confusion use the symbols η, η' to denote the elevations at the upper surface and at the interface, respectively. Hence, putting $y=0$ in (36), and $y=-h$ in (37), and combining the solutions, we have

$$\eta = -\frac{1}{g}(\sigma_1 A_1 \sin \sigma_1 t + \sigma_2 A_2 \sin \sigma_2 t) \cos kx, \quad . \quad . \quad . \quad (50)$$

$$\eta' = -\frac{1}{g}\left(\sigma_1 e^{-kh} A_1 \sin \sigma_1 t - \frac{\rho}{\rho'-\rho}\sigma_2 e^{kh} A_2 \sin \sigma_2 t\right)\cos kx. \quad (51)$$

Use has here been made of the relations (39), (43), (45). These formulæ correspond to the following initial distribution of ϕ, ϕ', viz.

$$\phi = \left\{ A_1 e^{ky} + A_2 \left(\cosh ky + \frac{\sigma_2^2}{gk}\sinh ky\right) \right\} \cos kx, \quad (52)$$

$$\phi' = \left\{ A_1 - \frac{\rho e^{2kh}}{\rho'-\rho}\frac{\sigma_2^2}{gk} A_2 \right\} e^{ky} \cos kx. \quad . \quad . \quad . \quad (53)$$

The coefficients A_1, A_2 are to be regarded as functions of k, depending on the particular manner in which the oscillation (of prescribed wave-length) is started. When it is necessary to call attention to this, they may be written as $A_1(k)$, $A_2(k)$.

The wave-trains due to a travelling disturbance are accordingly given, on the analogy of (21), by

$$\eta = -\frac{\sigma_1}{g(c-U_1)} A_1(\kappa_1) \sin \kappa_1 x - \frac{\sigma_2}{g(c-U_2)} A_2(\kappa_2) \sin \kappa_2 x, \quad (54)$$

$$\eta' = -\frac{\sigma_1 e^{-\kappa_1 h}}{g(c-U_1)} A_1(\kappa_1) \sin \kappa_1 x - \frac{\rho}{\rho'-\rho}\frac{\sigma_2 e^{\kappa_2 h}}{g(c-U_2)} A_2(\kappa_2) \sin \kappa_2 x, \quad (55)$$

where

$$\kappa_1 = \frac{g}{c^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

and κ_2 is the positive root of the equation

$$c^2 = \frac{g}{k} \cdot \frac{(\rho'-\rho)\sinh kh}{\rho'\cosh kh + \rho \sinh kh}. \quad . \quad . \quad (57)$$

It is also understood that in the preceding formulæ

$$\sigma_1 = \kappa_1 c, \quad \sigma_2 = \kappa_2 c. \quad . \quad . \quad . \quad . \quad (58)$$

If $c > c_0$, κ_2 is imaginary, and the second terms in (54) and (55) disappear.

The periods $2\pi/\sigma_1$, $2\pi/\sigma_2$ being different, the mean energies, and the mean rates of transmission of energy, in the two systems of waves may be calculated independently.

The potential energy, per unit length of the axis of x, being

$$\frac{1}{2}g\rho\eta^2 + \frac{1}{2}g(\rho'-\rho)\eta'^2, \quad . \quad . \quad . \quad . \quad (59)$$

the mean energies are

$$E_1 = \frac{2\kappa_1}{c^2}\left\{\rho + (\rho'-\rho)e^{-2\kappa_1 h}\right\}A_1^2(\kappa_1), \quad . \quad . \quad . \quad . \quad (60)$$

$$E_2 = \frac{\rho}{\rho'-\rho}\frac{\sigma_2^2 e^{2\kappa_2 h}}{2g(c-U_2)^2}\left\{\rho + (\rho'-\rho)e^{-2\kappa_2 h}\right\}A_2^2(\kappa_2). \quad (61)$$

The total wave-resistance is

$$R = R_1 + R_2, \quad . \quad . \quad . \quad . \quad . \quad (62)$$

where

$$R_1 = \frac{c-U_1}{c}E_1, \quad R_2 = \frac{c-U_2}{c}E_2. \quad . \quad . \quad (63)$$

Hence

$$R_1 = \frac{g}{c^4}\{\rho + (\rho'-\rho)e^{-2\kappa_1 h}\}A_1^2(\kappa_1), \quad . \quad . \quad . \quad . \quad (64)$$

$$R_2 = \frac{\rho}{\rho'-\rho}\frac{\sigma_2^2 e^{2\kappa_2 h}}{2gc(c-U_2)}\{\rho + (\rho'-\rho)e^{-2\kappa_2 h}\}A_2^2(\kappa_2). \quad (65)$$

6. As regards the determination of $A_1(k)$, $A_2(k)$, two special cases may be considered.

If an impulsive pressure $\cos kx$ be applied to the upper surface at the instant $t=0$, we have, initially,

$$\rho\phi = \cos kx \quad . \quad . \quad . \quad . \quad . \quad (66)$$

for $y=0$, and

$$\rho\phi = \rho'\phi' . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

for $y=-h$, the latter condition securing the continuity of the initial distribution of impulsive pressure. Hence from (52) and (53)

$$\rho(A_1 + A_2) = 1, \quad . \quad . \quad . \quad . \quad (68)$$

$$(\rho'-\rho)e^{-kh}A_1 - \rho\left(\cosh kh - \frac{\sigma_2^2}{gk}\sinh kh + \frac{\rho'e^{kh}}{\rho'-\rho}\frac{\sigma_2^2}{gk}\right)A_2 = 0. \quad (69)$$

With the help of (44), we find

$$A_1(k) = \frac{1}{\rho + (\rho'-\rho)e^{-2kh}}, \quad A_2(k) = \frac{(\rho'-\rho)e^{-2kh}}{\rho\{\rho + (\rho'-\rho)e^{-2kh}\}}. \quad (70)$$

Hence, in the case of a concentrated pressure travelling over the *upper* surface,

$$R_1 = \frac{g}{c^4 \{\rho + (\rho' - \rho) e^{-2\kappa_1 h}\}}, \quad \cdots \cdots (71)$$

$$R_2 = \frac{\rho' - \rho}{\rho} \cdot \frac{c}{2(c - U_2)} \cdot \frac{\kappa_2{}^2 e^{-2\kappa_2 h}}{g \{\rho + (\rho' - \rho) e^{-2\kappa_2 h}\}} \quad \cdot \quad (72)$$

Next, suppose that an extraneous impulsive force $\cos kx$ is applied downwards to an infinitely thin stratum at the interface. The initial conditions are now

$$\phi = 0 \quad \cdots \quad \cdots \quad (73)$$

for $y = 0$, and

$$\rho' \phi' - \rho \phi = \cos kx \quad \cdots \quad \cdots \quad (74)$$

for $y = -h$. Thus

$$A_1 + A_2 = 0,$$

and

$$(\rho' - \rho) e^{-kh} A_1 - \rho \left(\cosh kh - \frac{\sigma_2{}^2}{gk} \sinh kh + \frac{\rho'}{\rho' - \rho} e^{kh} \frac{\sigma_2{}^2}{yk} \right) A_2 = 1. \;(75)$$

Hence

$$A_1(k) = -A_2(k) = \frac{e^{-kh}}{\rho + (\rho' - \rho) e^{-2kh}} \quad \cdots \quad (76)$$

The comparison with (70) shows, as we should expect, that the second type of waves is now favoured relatively to the first.

In the case of a concentrated vertical force travelling along the *interface* the two components of the resistance are accordingly

$$R_1' = \frac{g e^{-2\kappa_1 h}}{c^4 \{\rho + (\rho' - \rho) e^{-2\kappa_1 h}\}}, \quad \cdots \cdots (77)$$

$$R_2' = \frac{\rho}{\rho' - \rho} \cdot \frac{c}{2(c - U_2)} \cdot \frac{\kappa_2{}^2}{g \{\rho + (\rho' - \rho) e^{-2\kappa_2 h}\}} \quad \cdot \quad (78)$$

It is to be remembered in these problems that R_2 and R_2' vanish when $c > c_0$.

The formulæ as they stand are open to the objection that they make some part of the resistance increase indefinitely as c is diminished. Thus (71) makes $R_1 = \infty$ for $c = 0$, whilst (78) makes $R_2' = \infty$ under the same condition. This paradoxical result is easily understood if we remember that we have imagined a finite force to be concentrated on an

infinitely narrow area. To get anything like a representation of real conditions we must suppose the force to be diffused to some extent. Mathematically, this is most easily attained by introducing a factor e^{-kb} under the integral signs in (2), and making the consequent changes in the subsequent formulæ. The effect is that the pressure is now distributed on each side of a central line according to the law

$$\frac{b}{\pi(b^2 + x^2)}, \quad \cdots \quad \cdots \quad (79)$$

the intensity falling to half the maximum when $x = \pm b$.

In this way we find, for a disturbance advancing along the upper face,

$$R_1 = \frac{ge^{-2\kappa_1 b}}{c^4 \{\rho + (\rho' - \rho)e^{-2\kappa_1 h}\}}, \quad \cdots \quad \cdots \quad (80)$$

$$R_2 = \frac{\rho' - \rho}{\rho} \frac{c}{2(c - U_2)} \frac{\kappa_2^2 e^{-2\kappa_2 h - 2\kappa_2 b}}{g\{\rho + (\rho' - \rho)^{-2\kappa_2 h}\}}; \quad (81)$$

whilst for a disturbance travelling along the interface

$$R_1' = \frac{ge^{-2\kappa_1 h - 2\kappa_1 b}}{c^4 \{\rho + (\rho' - \rho)e^{-2\kappa_1 h}\}}, \quad \cdots \quad \cdots \quad (82)$$

$$R_2' = \frac{\rho}{\rho' - \rho} \frac{c}{2(c - U_2)} \frac{\kappa_2^2 e^{-2\kappa_2 b}}{g\{\rho + (\rho' - \rho)e^{-2\kappa_2 h}\}}. \quad (83)$$

7. The name "dead-water" is given to a phenomenon occasionally observed in Norwegian fiords, and other similar localities, where the sea is covered by a stratum of fresh water brought down by rivers. It consists in an abnormal resistance experienced by slowly sailing vessels, which disappears if the speed can be raised above a certain limit. The vessel appears to be gripped by some mysterious power, and cannot be properly handled.

The matter was brought by Nansen to the notice of V. Bjerknes, who attributed the phenomenon to the interfacial waves generated at the common boundary of the fresh and salt water. At his suggestion the question was taken up by Ekman, who has devoted a long memoir[*] to the subject. This includes descriptive accounts from various

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[*] 'Scientific Results of the Norwegian North Polar Expedition,' 1893–96, pt. 15. (Christiania, 1904.)

sources, and an account of tank experiments made in verification of the above explanation. There are also some indications of mathematical theory. A fuller publication was promised : but I do not know whether this has taken place.

From the theoretical point of view the matter is not altogether a simple one. The difference of densities is actually very small, and although interfacial waves of considerable amplitude may be readily generated, their energy for given amplitude is relatively slight. It is obvious, in fact, that if the difference be small enough no appreciable effect of the kind contemplated could be expected, since the case would be practically that of a homogeneous fluid. It is difficult to devise a case which shall admit of mathematical treatment, and at the same time be comparable with actual conditions; but in default of this we may examine whether any indications can be gathered from the preceding formulæ.

In the phenomena referred to the ratio $(\rho' - \rho)/\rho$ has some such value as $\frac{1}{40}$. The expressions

$$\rho + (\rho' - \rho)e^{-2\kappa_1 h}, \quad \rho + (\rho' - \rho)e^{-2\kappa_2 h},$$

which occur in our formulæ, may therefore be replaced without sensible error by ρ. The values of R_1 and R_1' in (80) and (82) are therefore practically the same as if the fluid had been homogeneous.

Since $g^2/c^4 = \kappa_1^2$, we have from (80) and (81)

$$\frac{R_2}{R_1} = \frac{\rho' - \rho}{\rho} \frac{c}{2(c - U_2)} \left(\frac{\kappa_2 b e^{-\kappa_2 b}}{\kappa_1 b e^{-\kappa_1 b}} \right)^2 e^{-2\kappa_2 h}, \quad . \quad . \quad (84)$$

approximately. A glance at the numerical table at the end of this paper, which is calculated on the basis of $(\rho' - \rho)/\rho = \frac{1}{40}$, shows that for values of c in the neighbourhood of $\frac{1}{2}c_0$ this ratio may be enormous, in spite of the smallness of the first factor, if b be at all comparable with h. That is, even when the disturbing pressure acts on the upper surface, the resistance due to the interfacial waves may greatly exceed that (in itself very small) due to the waves on the upper surface.

When the disturbing forces act at the interface this resistance is again greatly increased; thus from (81) and (83)

$$\frac{R_2'}{R_2} = \left(\frac{\rho}{\rho' - \rho} \right)^2 e^{2\kappa_2 h} \quad . \quad . \quad . \quad . \quad (85)$$

Ekman's experiments showed, in fact, that the resistance was greatly increased when the bottom of his model boat approached or penetrated the surface of separation.

As regards the actual magnitude of the resistance, an estimate, necessarily somewhat vague, can be made in a certain case as follows: It has been computed * that the wave-resistance to a horizontal cylinder of radius a towed at right angles to its length with velocity c, at a depth h in homogeneous fluid, is

$$R = 4\pi^2 g\rho a^4 \kappa_1^2 e^{-2\kappa_1 h}, \quad . \quad . \quad . \quad . \quad (86)$$

where $\kappa_1 = g/c^2$ as before. If we assume that when the cylinder is towed along the interface the wave-resistance at the interface bears to that at the upper surface the ratio of R_2' to R_1', as found from (82) and (83), we get

$$R = \frac{\rho}{\rho' - \rho} \cdot \frac{c}{2(c - U_2)} \cdot 4\pi^2 g\rho a^4 \kappa_2^2 . \quad . \quad . \quad (87)$$

To make the formulæ more comparable, we have put $b = 0$, which involves an under-estimate, and leads to no difficulty for values of c in the neighbourhood of $\frac{1}{2}c_0$. Thus if we put $\kappa_2 h = 2$, and $h = 250$ cm., which was the estimated thickness of the freshwater layer in one of Nansen's experiences, we find

$$R = \cdot 11 a^4, \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

in grammes per centimetre of length of the cylinder. This corresponds to a speed

$$c = \cdot 498 c_0 = 39 \text{ cm./sec.,}$$

or about 1·4 kilometres per hour.

Considering the somewhat precarious nature of the above comparison, no importance can be attached to the precise numerical value obtained for R; but the order of magnitude of the result (which almost certainly errs in defect) seems decidedly to support the adequacy of the theory advanced by Bjerknes and Ekman.

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* *Annali di matematica* (3) vol. xxi. p. 327 (1913).

$\kappa_2 h$.	c/c_0.	$\kappa_1 h$.	λ_2/h.	λ_1/h.	$\frac{1}{2}c/(c-\mathrm{U}_2)$.	$(\kappa_2 h e^{-\kappa_2 h})^2$.
10	·225	790	·628	·008	1·00	$2\cdot13\times10^{-7}$
5	·318	395	1·26	·017	1·00	$1\cdot07\times10^{-3}$
4	·356	316	1·57	·020	1·00	$5\cdot39\times10^{-3}$
3	·410	224	2·09	·028	1·02	$2\cdot23\times10^{-2}$
2	·498	161	3·14	·039	1·08	$7\cdot32\times10^{-2}$
1·5	·566	125	3·53	·050	1·19	$1\cdot12\times10^{-1}$
1	·661	91·6	6·28	·069	1·46	$1\cdot35\times10^{-1}$
·8	·710	79·4	7·86	·079	1·69	$1\cdot29\times10^{-1}$
·6	·766	68·1	10·5	·092	2·09	$1\cdot08\times10^{-1}$
·4	·833	57·7	15·7	·109	3·08	$7\cdot19\times10^{-2}$
·2	·910	48·3	31·4	·130	5·45	$2\cdot68\times10^{-2}$
·1	·953	44·0	62·8	·143	10·57	$8\cdot19\times10^{-3}$

The symbols λ_1, λ_2 denote the lengths of the waves at the upper surface and at the interface, respectively.

XLV. *The Theory of the Winds.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a recent paper * I suggested that the reason why the winds of middle latitudes blow as a general rule towards the poles, in opposition to the surface temperature gradient, is that the stratosphere is much warmer over high latitudes than it is over low latitudes. If the winds blew in accordance with the surface-temperature gradients, there would be north-easterly and south-easterly winds moving from the poles towards the equator, and the equatorial regions would be areas of low pressure whilst the polar regions would be areas of high pressure—the high-pressure belts which are now at latitudes 30° north and 30° south of the equator would move to the poles. Such a distribution of the winds would result in a very considerable increase in the size of the frigid polar areas.

Dr. Walker has recently suggested that the effect of solar radiation on the upper atmosphere may be an important consideration.

The comparatively high temperature of the stratosphere over the polar areas is not accounted for very easily. In the summer, no doubt, the atmosphere in these areas enjoys continuous sunshine, and for some time receives more heat

* Phil. Mag. vol. xxx. July 1915, pp. 13–33.

than does the equator ; but the reverse holds good in the winter, yet the winter as well as the summer temperature of the stratosphere above the poles is higher than it is above the equator.

One suggestion * made was that the high temperature of the stratosphere may be due to the presence in it of ions and meteoric dust.   But it is necessary to suppose that these are most numerous in high latitudes.

That ions exist in the upper atmosphere is now considered to be very probable.   Prof. H. Nagaoka suggests that they may result from two causes.   The first cause is the ultra-violet light of the sun, which he believes is capable of ionizing the atmosphere down to about 40 kilometres from the earth's surface.   The second is the stream of electrons emitted by the sun.   These electrons according to Arrhenius would be caught by the earth's magnetic lines of force and would be deflected in long spirals along the lines to the poles. Some heating of the atmosphere may result from their loss of velocity on reaching the atmosphere.   They may also arrest some of the sun's heat for the following reasons.

At ordinary temperatures ions load themselves by attracting surrounding molecules of gas.   They thus form complexes consisting of as many as thirty molecules.   Such groups of molecules may possibly arrest rays other than the ultra-violet ones, and raise the temperature of the gas in which they move. I am not aware, however, that any experiments have been made to ascertain the effects, if any, ions have on radiant heat.

The variations which take place in the direction of the flow of the winds from time to time seem to demand some variable cause.   Both the quantity of meteoric dust, and the number of ions in the stratosphere, no doubt vary from time to time.

If ions can intercept the heat of the sun or warm the atmosphere by impact as they reach it, and owing to the magnetic field of the earth are deflected towards the poles, the comparatively high temperature of the stratosphere over high latitudes might be accounted for.

Yours very truly,

R. M. DEELEY.

Abbeyfield,
Salisbury Avenue,
    Harpenden.
        Feb. 15, 1916.

* Ibid. p. 31.

XLVI. *The Variation of the Radioactivity of the Hot Springs at Tuwa. By* A. Steichen, *S.J., Ph.D., Professor of Physics, St. Xavier's College, Bombay* *.

IN his interesting paper contributed to this Journal †, Professor R. R. Ramsey gives two instances of the variation of the emanation-content of springs. He finds the greater radioactivity at the time when the springs are yielding the greater amount of water. My experience with a highly radioactive spring here in India is just the opposite.

Tuwa is a village in the Kaira District, Bombay Presidency, 319 miles north of Bombay. The geographical coordinates of the place are lat. $22° 43'$, long. $73° 30'$. Not far from the railway-station at Tuwa there is a small area, about 20 by 17 metres, where numerous hot and cold springs issue from the ground. The highest temperature of the springs which I measured is $67° C.$, the lowest $28° C.$

On the 13th December, 1910, the Rev. H. Sierp and myself measured the radioactivity of the hottest and of the coldest springs ‡. The method of measurement was the Schmidt shaking method ; the instrument used was a Wulf quartz-fibre electroscope with an ionization-chamber. We applied Duane's correction for the absorption of rays by the walls of the cylindrical condenser §. The radioactivities are calculated by means of Laborde's empirical values ‖. All the measurements were made at the springs.

We obtained the following results :—

Hot spring :

Saturation current ...... 82·1 Mache units (M.U.).
Radioactivity .... $33·00 \times 10^{-9}$ curie (C.).

Cold spring :

Saturation current...... 84·25 M.U.
Radioactivity........... $33·88 \times 10^{-9}$ C.

On the 11th April, 1911, we visited the springs once more, in order to ascertain whether the radioactivity of the

* Communicated by the Author.
† Phil. Mag. vol. xxx. pp. 815–818 (1915).
‡ Indian Medical Gazette, December 1911.
§ Kohlrausch, *Lehrbuch der Prakt. Physik*, 11th ed. p. 657.
‖ Laborde in *Handbuch der Radium-Biologie und Therapie*, p. 41.

water had undergone a change. We found that the supply of water from the springs was considerably less than in December 1910. There had been no rain during December, January, February, March, and April. The actual strength of the flow, however, was not measured. The radioactivity of the hot spring was examined in the same way and with the same instrument as in December 1910. We obtained the following results :—

> Saturation current............ 154·37 M.U.
> Radioactivity.................. $62·06 \times 10^{-9}$ C.

Thus the radioactivity of the hot spring was almost double of what it had been in December. For want of time the cold spring was not examined on this occasion.

Here, then, we find the greater radioactivity when the spring yields less water. This result can be accounted for by considering the local conditions.

The cold spring showed practically the same radioactivity as the hot spring. This seems to indicate that at Tuwa the radium-bearing rock is near the surface, as the cold spring is not likely to come from a great depth.

Moreover, the radioactivity of the neighbouring wells decreases with their distance from the springs. Three wells were examined for radioactivity in April 1911[*].

1st well. Distance from the hot spring about 200 metres.

> Saturation current............ 19·85 M.U.
> Radioactivity .... $7·98 \times 10^{-9}$ C.

2nd well. Distance from the hot spring about a quarter of a mile.

> Saturation current............ 8·1 M.U.
> Radioactivity .... $3·26 \times 10^{-9}$ C.

3rd well. Distance from hot spring about half a mile.

> Saturation current..... ...... 7·2 M.U.
> Radioactivity.................. $2·89 \times 10^{-9}$ C.

We cannot lay much stress on the difference between the second and the third well. The difference in their radio-activities can be fully accounted for by the fact that the second well was not much used, whereas the third well, which is situated at the railway-station, was much resorted to. One result, however, stands out quite clearly : there is a distinct drop in the radioactivity of the water as we move away from the hot spring. This seems to justify the con-

clusion that the radium-bearing layer either does not extend for a great distance from the springs in the direction of the wells, which were all on the same side of the springs, or that the layer slopes down to a greater depth. Thus the supply of emanation seems to come mainly from a relatively limited area.

If we make the assumption that the supply of emanation is constant throughout the year, then the greater radioactivity when the springs yield little water is to be attributed to a greater concentration of the emanation in the water. When the output of water is greater, then the same, or almost the same, amount of emanation is absorbed by a greater quantity of water, the solution becomes more dilute, and we get a smaller radioactivity of the water.

From Professor R. R. Ramsey's results and my own observations, it follows that we cannot draw a conclusion *à priori* as to the variation of the emanation-content of a given particular spring with the change in the flow of water. The connexion between the two quantities depends on local conditions. Experiment alone can decide what that particular connexion is in a given case.

Summary.

The radioactivity of the hot spring at Tuwa is less when the spring yields much water than when the supply of water is relatively small.

This behaviour of the spring does not disprove Professor R. R. Ramsey's results. It can be explained by local conditions.

Physical Laboratory,
St. Xavier's College, Bombay.
1st January, 1916.

XLVII. *On the High Frequency Spectra of the Elements Gold– Uranium. By* Manne Siegbahn, *Dr. phil., and* Einar Friman, *Lic. phil.**

1. IN the X-ray spectra we have, as well known, a reliable method of determining the ordinals of the elements, and hence a method of detecting missing elements. Thus, for instance, Moseley[†], in his excellent researches on the

* Communicated by the Authors.
† Phil. Mag. [6] vol. xxvii. p. 703 (1914).

high frequency spectra, has shown that between aluminium and gold only three elements, hitherto not detected, are to be expected.

This investigation aims at a determination of the elements between gold and uranium. Some temporary measurements in this region have already been made by de Broglie* after the secondary radiation method. A research of lead also has been made by Rutherford and Andrade †, using the γ rays from an emanation-tube as primary radiation.

As in this case, however. a relatively large gap (of 6 elements) is to be passed over, measurements much more accurate than those of de Broglie are necessary. Our plates of the X-ray spectra, therefore, are taken by the primary radiation method, that is, the element in question was placed as anticathode in an X-ray tube. As, further, the wave-length space under examination, the α-lines of the L-series, consists of slightly absorbable rays, the tube was furnished with a window of 0·05 mm. of aluminium.

In this first research we have only determined one line for every element, and this the strongest of the two α-lines of the L-series. This group also is the best known of the four forming the L-series in Moseley's research. His investigation extended from zirconium to gold. By this research the measurements thus are extended over more than 50 elements.

2. In the spectrometric investigation a rotating rock-salt crystal was used, the rotatory speed of which was about 1° in 4 min. Thereby every space was gone over several times (between 4 and 16) according to the intensity of the rays. As diaphragms (collimator) two lead slits were used, the first with a width of 0·1 or 0·2 mm., the second of 1–2 mm. The distances first slit-crystal and crystal-plate were equal (about 13 cm.).

Of the elements examined, gold as thin sheet was soldered on the copper anticathode, thallium, lead, and bismuth melted on the *tinned* copper plate, mercury (as cinnabar), thorium (as thorium oxide), and uranium (as metal powder) rubbed on the copper plate, scratched with a rough file.

The tube was evacuated with a molecular air-pump.
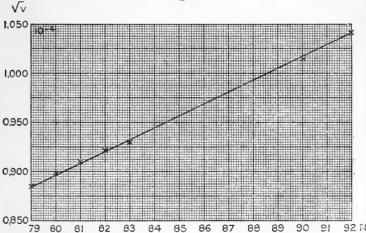
3. The results of the measurements are given in the following table :—

* *C. R.* 1914.
† Phil. Mag. [6] vol. xxvii. p. 854 (1914).

Element.	Ordinal. N.	Wave-length. $\lambda_{\alpha_1} \cdot 10^8$ cm.	$\sqrt{\dfrac{1}{\lambda}} = \sqrt{\bar{\nu}}$ $\times 10^{-4}$.	$Q_R = \sqrt{\dfrac{\nu}{\frac{5}{36}\nu_0}}$.	$N - Q_L = b$.
Au	79	1·280	0·884	71·6	7·4
Hg	80	1·243	0·897	72·7	7·3
Tl	81	1·209	0·909	73·7	7·3
Pb	82	1·179	0·921	74·6	7·4
Bi	83	1·144	0·935	75·7	7·3
. . . . .	. . . .				
Th	90	0·971	1·015	82·2	7·8
. . . . .	. . . .				
U	92	0·919	1·043	84·5	7·5

The graphic representation of the values $\sqrt{\dfrac{1}{\lambda}} = \sqrt{\bar{\nu}}$ in fig. 1 shows that thorium as 90 and uranium as 92 give a linear relation between $\sqrt{\nu}$ and N. This succession of the

Fig. 1.

heaviest elements perfectly agrees with the system of J. R. Rydberg [*]. A numerical comparison of the values after the relation given by Moseley,

$$N - \sqrt{\dfrac{\nu}{\frac{5}{36}\nu_0}} = b, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

shows further that our values agree very well with those

* Lunds Univ. Årsskr. N. F. Afd. 2, Bd. 9. Nr. 18, 1913.

found by him for the other elements (where b on an average $= 7\cdot4$). The results also do not admit of any doubt as to the place of the different elements.

A calculation of the whole L_{α_1}-group hitherto known shows besides, that the formula (1), theoretically set up by Moseley, does not give the best representation of the experimental values. If (1) is written in the form

$$\sqrt{\nu} = a[\mathrm{N} - b], \quad \ldots \ldots \quad (2)$$

the calculation for b gives the value $7\cdot12$ ($a = 122\cdot8$ instead $123\cdot4$ by Moseley). A divergence from the *linear relation* given in (2) between $\sqrt{\nu}$ and N does not seem to take place within the examined domain of 52 elements.

For the present may be noticed, that the second line of the doublet (α_2), for instance, of thallium has a wave-length of $\lambda_{\alpha_2} = 1\cdot220$ ($\lambda_{\alpha_1} = 1\cdot209$).

Physical Laboratory,
 University of Lund,
  Dec. 1915.

XLVIII. *Notices respecting New Books.*

The Tutorial Algebra (Advanced Course). Based on the Algebra of Radhakrishnan. By WILLIAM BRIGGS, LL.D., M.A., B.Sc., F.R.A.S., and G. H. BRYAN, Sc.D., F.R.S. London: W. B. Clive. University Tutorial Press. 1913.

TEXT-BOOKS on Algebra are, in these days, as plentiful as blackberries, and it must be no easy matter discriminating among them. Each doubtless has its peculiar virtues; but all of the same standard must cover much the same ground, discuss the same methods in much the same way, and append to each chapter appropriate examples for the student to sharpen his wits on. The authors of the Tutorial Algebra, now in its fourth edition, have certainly satisfied all the requirements of a sound treatise, and have placed in the hands of the intermediate student a book, the careful study of which will bring him up to the threshold of higher mathematics. The book assumes a knowledge of elementary algebra up to the solution of quadratic equations; and the scope of the treatment may be inferred from the enumeration of a few of the headings of the later chapters, such as progressions and series, logarithms, permutations, combinations, complex quantities, determinants, continued fractions, and so on. The historic foot-note on page 219, dealing with the discovery of logarithms, hardly brings out the facts of the case as recorded by Briggs himself. See Professor G. A. Gibson's article on "Napier's Logarithms and the Change to Briggs's Logarithms," recently published in the 'Napier Tercentenary Memorial Volume.'

A New Analysis of Plane Geometry, Finite and Differential, with numerous Examples. By A. W. H. THOMPSON, B.A. Cambridge University Press, 1914.

IN this analysis points are represented by small Roman letters and straight lines by small Greek letters. The symbol $\overline{ab}$ represents the line joining a and b; and $\overline{\alpha\beta}$ represents the point of intersection of the lines α and β. The distance between a and b is denoted by (ab); the angle between α and β by $(\alpha\beta)$; the perpendicular distance from a on β by $(a\beta)$. The expression $(\overline{ab}\gamma d)$ means the distance of the point d from the intersection of the line $\overline{ab}$ with the line γ. The expression $\sin(\overline{\alpha\beta}c\delta)$ means the sine of the angle which the line δ makes with the line joining the intersection of the lines $\alpha\beta$ and the point c. The symbol (abc) is twice the area of the triangle formed by the points; it may be written $|(ab)|(\overline{abc})$, which means the product of the length of the line joining a and b and the perpendicular distance from the point c on the line $\overline{ab}$. Also the symbol $(\alpha\beta\gamma)$ is defined as $\sin(\alpha\beta).(\overline{\alpha\beta}\gamma)$. A suffix notation is introduced to represent the vectorial construction by which one point is got from another; and by consideration of the consecutive positions of a moving point and of a moving line a new Differential Geometry is obtained. The tangential line to the curve at the point x is represented by τx, and the normal to the curve at the point x by νx, so that $(\tau x \nu x) = \pi/2$. Similarly the expression pξ represents the point of intersection of the line ξ and its consecutive position ξ'. The curvature at the point x may be written either as the differential coefficient of τx or of νx with respect to x, and is represented by ρx. Some of these notations are suggestive, as the author himself points out, of Grassmann's methods; but the whole development is quite different and essentially new. The author is to be congratulated upon the invention of a system of symbolic plane geometry which expresses results and demonstrates theorems by a general process built upon the analytical recognition of the elements of position and displacement. The book is beautifully printed, and into its 118 pages there is packed a vast amount of geometrical fact.

The Algebra of Logic. By LOUIS COUTURAT. Authorized English Translation by LYDIA GILLINGHAM ROBINSON, B.A. With a Preface by PHILIP E. B. JOURDAIN, M.A. (Cantab.). Chicago and London. The Open Press Publishing Company. 1914.

THE mathematical analysis of logic originated with George Boole (1847) and was developed in his later work on the Laws of Thought (1854). Ernst Schröder in 1877 and Alexander Macfarlane in 1879 continued the investigations along somewhat similar lines,

and in the former's three-volumed treatise on the Algebra of Logic (1890, 1891, 1895) the whole Boolian method is perfected. It is this method which is expounded by Couturat concisely and clearly in a book of 92 pages. Although the calculus was devised to express the principles of reasoning, it may be developed from the formal point of view as an algebra based upon certain assumed axioms. This may be done without any attempt to interpret the results as corresponding to actual operations of mind, or to apply them to logical problems. Such, broadly speaking, is the aim of Couturat in his dainty treatise. He treats the calculus as a form of algebra and not as logic. The translation has been admirably done; it is difficult to imagine that the original French could be more lucid and more exact than in its English dress. It is sad to realize that nothing more will come from the hand of this gifted French author, who lost his life by an accident in the early months of the war.

Practical Physical Chemistry. ALEX FINDLAY, M.A., Ph.D., D.Sc. Third Edition enlarged. Longmans, Green & Co., 1914. Price 4s. 6d. net.

IN this third edition of a very useful manual several fresh subjects and new experimental methods have been added, such as the determination of vapour densities by the methods of Blackman and of Menzies, and the application of vapour-density determinations to the analysis of binary mixtures of normal liquids; application of vapour-pressure measurements to the determination of molar weight; determination of minute solubilities and of hydrolysis by conductivity measurements, &c. References to original literature have been added to most of the chapters, and an appendix has been inserted giving tables of some of the more important physical data relative to the subject.

Elements of Optics for the use of Schools and Colleges. GEORGE W. PARKER, M.A. Pp. 122. London, New York, & Bombay : Messrs. Longmans, Green & Co. Price 2s. 6d.

THERE is not very much to be said about this little book. It describes in a very simple manner, involving only algebra and elementary trigonometry, the fundamental phenomena of geometric optics. The author claims to have endeavoured to make the book as attractive as possible; it contains little, however, besides the outlines of mathematical proofs. No attempt has been made to add to the attractiveness and educational usefulness of the book by describing experiments which the pupil might make for himself. No subject lends itself more readily to simple experimental treatment than the subject of light. A lens, a prism, a plane and a concave mirror, and a few pins are all the apparatus

necessary. The omission of such experimental detail is scarcely pardonable. The diagrams are usually clear : that one illustrating dispersion is, however, misleading, and the sectional drawing of the eye seems unnecessarily crude. The refraction by the eye is attributed entirely to the lens ; perhaps the author would be astonished to be told that two-thirds of the total refraction occurs at the front surface of the cornea : the lens is a comparatively unimportant organ. It may be doubted whether the gradation of density in the lens is " an admirable provision of nature which ensures that no light is lost by total reflexion." There would be so little difference of index between the lens and the two humours if no gradation existed, and consequently so little reflexion, that its diminution would be of no importance in view of the fact that the chief loss by reflexion also takes place at the anterior surface of the cornea.

Plane Trigonometry, an Elementary Text-book for the Higher Classes of Secondary Schools and for Colleges. By H. S. CARSLAW, Sc.D. (Camb.), D.Sc. (Glasg.). Macmillan & Co. London, 1915.

THE first edition of this book appeared in 1909, and was the embodiment of the methods which Professor Carslaw had gradually adopted during his experience as a teacher first in Glasgow and then in Sydney. The present edition differs only in slight details from its predecessor, the most important innovation being the indication of the harder portions by means of asterisks. The book is divided into two Parts, the first part containing within its twelve chapters the ordinary elementary trigonometry, which gives the trigonometrical ratios and their simpler transformations and culminates in the solution of triangles and the measurement of heights of inaccessible objects. In Chapter XII the radian is introduced for the first time and an interesting discussion given of the meaning of the length of a curve. There is also a somewhat isolated section on the Dip of the Horizon, in which no hint is given that the simple calculated result is not in accord with observation on account of refraction of light. Chapter XIII, which opens Part II, is devoted to the properties of triangles and their related circles, a kind of mathematical *cul de sac* which some geometrical minds spend their existence in exploring. The remaining chapters introduce the student to quite a different atmosphere, through which he should pass ere long into the æthereal regions of infinite series and function theory. Professor Carslaw intentionally limits his treatment to the Real ; and yet a slight hint now and then might stimulate the intelligent student by giving him a vision of the Imaginary splendours behind the curtains of reality. These limitations, however, in no way detract from the value of the book as a sound exposition of the subject.

Radium, X-rays, and the Living Cell; with Physical Introduction. By HECTOR A. COLWELL, M.B., D.P.H., and SIDNEY RUSS, D.Sc. London : G. Bell & Sons, Ltd.   1915.

THE main object of this volume has been to describe the established facts in regard to the effects that X-rays and the rays from radium have upon living cells.   But in order to do this intelligibly it has first been necessary to give a summary account of these rays from the physical point of view.   The mass of material available is now so great that this summary is unavoidably very curt ; but the attempt has been successfully made to give an outline of those multifarious facts which will put the medical man into touch with the properties of the physical agent with which he has to deal. It was time that such an attempt should be made, and the fact that it has been made by Dr. Russ is sufficient guarantee that it has been authoritatively made.   The general impression left is the need for much more experimental work to be done even on the physical side.   Measurements of X and other rays are necessarily physical measurements, and it cannot be said at present that the medical man has yet been provided with a satisfactory means of determining how much and what kind of these rays he is utilizing.   So important is the point that we think the authors might with advantage have given more space to it.

The action upon the living cell is somewhat outside the scope of this Magazine.   There is one part, however, which deserves serious mention, viz. that dealing with the dangers attending the use of these rays.   Physical investigators, as a rule, no doubt take even superabundant precautions against dangerous physiological consequences to themselves ; but even to them a fuller knowledge of what these dangers are may not be without benefit. To the large number of amateur workers the warning is urgently needed ; and it may be hoped that this work will fall into their hands.

We wish the volume success ; it is a marked advance on anything that has appeared previously.

The Limitations of Science.   By LOUIS TRENCHARD MORE, Ph.D., Professor in the University of Cincinnati.   London : Constable & Company Ltd.   New York : Henry Holt & Company. 1915.

IN this book, whose seven chapters appeared originally in somewhat shorter form as separate essays in various journals, the author gives an unsparing criticism of the modern tendency to metaphysical hypothesis.   As explained in the brief preface, the continuity of the whole was planned from the beginning.   The motto chosen by Professor More is the famous passage from Newton opening with the words "Hypotheses non fingo."   The scientific man may make as many hypotheses as he pleases in order to get behind some established law of Nature ; but he should never forget that they are hypotheses.   From lack of clear philosophic thinking there is a tendency in some quarters to confuse

hypotheses with natural laws. Some have even gone the length of imagining that we know more about the atom, of whose existence we have no direct experimental evidence, than we do about sensible matter. Such a statement is true in the sense that the atom possesses only those properties which we ascribe to it. But after all, it is merely a creation of the imagination; whereas if science is to exist at all, sensible matter must be regarded as having an objective existence. Descartes, Poincaré, J. J. Thomson, Larmor, Lorentz, Einstein, Minkowski, and others are cited as having in greater or less degree fallen into this kind of fallacy. The contradictions and inconsistencies show that there is something wrong. One denies the existence of an æther, another speaks of matter as being probably a hole in the æther. In a universe in which all motion is purely relative, light is assumed to have an absolute constant velocity in all regions devoid of matter. The ratio (e/m) of the charge on an electron to the mass associated with it is found to vary with the velocity. The general assumption is that the charge is constant—an assumption suggested by the facts of electrolysis; hence it must be the mass which varies. But, asks Professor More, why should we not assume the charge to vary and the mass to remain constant? These remarks will give some idea of the purpose and scope of the book. It is well and clearly written, and is an appeal to scientific men to give philosophical thinking a place in their physical and metaphysical scheme. True science has its limitations; and whatever scientific readers may think regarding some of the arguments advanced, the great majority will be in thorough sympathy with the sane outlook of the author in respect of the so-called science of Eugenics, as shown forth in the last chapter.

XLIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxx. p. 448.]

March 24th, 1915.—Dr. A. Smith Woodward, F.R.S., President, in the Chair.

THE following communication was read :—

'The Stratigraphy and Petrology of the Lower Eocene Deposits of the North-Eastern Part of the London Basin.' By Percy George Hamnall Boswell, B.Sc., F.G.S.

The following divisions of the Lower Eocene occur in the area :—

> London Clay—Basement-bed only
> The Pebble-Beds and accompanying sands.
> Reading Beds.
> Thanet Beds.

The unconformity of the Eocene upon the Chalk is discussed, and reasons are given for regarding the layer of green-coated flints

at the bottom of the Thanet Beds in the area as a true basal con-
glomerate. The Eocene deposits overstep the Chalk zones from
the zone of *Ostrea lunata* to that of *Micraster cor-anguinum,* and
also transgress the Chalk surface-contours ; owing to the greater
dip of the base of the Eocene, the latter also bevels off the zones
in South-Eastern Suffolk.

Evidence is adduced to show that the London Clay overlaps the
Lower London Tertiaries, and rests directly upon the Chalk in
Norfolk. The Reading Beds also overlap the Thanet Beds in the
western part of the area. A hypsometrical map of the Chalk-
surface in the London Basin is presented, and a minimum estimate
of the unconformity, in terms of thickness of Chalk removed, is
given for the northern part of the basin.

Isopachytes for the London Clay and Lower London Tertiaries
(the north-western feather-edge of each deposit being the zero
isopachyte) have been plotted, and since the beds thicken on each
side of a central area in South-Eastern Suffolk, where the sub-
Eocene Chalk-surface gradient is least, the curves are seen to be
convex to a central axis. The Chalk zones, Chalk surface-contours,
Lower London Tertiaries, and London Clay successively change
strike as they are traced north-eastwards. The instability over
the axis, which may be of Charnian trend, took the form of an
earth-ripple forced north-eastwards, throughout Eocene times,
towards that part of East Anglia where the Palæozoic platform
rises. The unconformity of the Pliocene deposits upon the Eocene
and the Chalk is shown to be significant in this connexion.

Stratigraphical details of the various divisions and descriptions
of new sections are given. Tables of mechanical analyses (obtained
by elutriation) throw light on the conditions of deposition, and
permit of the adoption of an exact terminology. The visible
Thanet Beds are of two facies : (*a*) the Ipswich or Eastern type,
with predominant green clays, and (*b*) the Sudbury or Western
type, characterized by the prevalence of light-coloured sands.

The variations in lithology of the Reading Beds are described,
and it is shown that the Pebble-Beds belong lithologically and
petrologically to the Reading Beds, but that their scanty fauna
is a London Clay one. The fauna of the London Clay is also
enumerated, and the author is of the opinion that the bed was
deposited under isostatic conditions accompanying a sagging on
each side of the central axis mentioned above.

The distribution of the sarsens in the area is plotted out on a
map, and their petrology is considered ; it is concluded that, in
this district, they are derived from the sands of the Reading Beds.

The mineral constitution of the various divisions of the Eocene
Beds is discussed in detail. The mineral assemblage is seen to
conform to one type throughout (characterized by abundant small,
angular, colourless garnets, also by staurolite, tourmaline, and
kyanite), but differences occur which allow of the beds being easily
distinguished one from the other. There is remarkable constancy in

mineral composition over wide areas, and in deposits lithologically different. The mineral suite of the succeeding Pliocene beds (with abundant red garnets, andalusite, mica, and ferromagnesian minerals) is shown to be very different, and the constituents of various other East Anglian deposits are also compared.

In the Thanet Beds, ferromagnesian minerals are present and undecomposed, the micas being rare. In the shallow waters in which the Reading Beds were deposited, the biotite, hornblende, pyroxene, and epidote appear to have been largely lost, aided no doubt by current-drift along a shore. The Pebble-Beds show occasionally natural concentration of heavy minerals by oscillatory current-action. In the subsidence which followed when the London Clay was deposited, muscovite and biotite appeared in fair quantity, and hornblende became abundant. Such minerals as magnetite, ilmenite, rutile, zircon, glauconite, etc., are plentiful throughout.

April 14th.—Dr. A. Smith Woodward, F.R.S., President,
in the Chair.

The following communication was read :—

'Further Observations upon the Late Glacial, or Ponder's End, Stage of the Lea Valley.' By Samuel Hazzledine Warren, F.G.S. With Notes on the Mollusca by Alfred Santer Kennard, F.G.S., and Bernard Barham Woodward, F.L.S., F.G.S.

The paper is supplementary to that previously published (Q. J. G. S. vol. lxviii, 1912, p. 213), and describes additional sections which increase the range of the deposits. They have now been traced, with the assistance that the author has received from Mr. A. Wrigley, for a distance of $6\frac{1}{2}$ miles along the valley and $2\frac{1}{4}$ miles across it. The section at Hedge Lane, Lower Edmonton, shows several thick, and for the most part undisturbed, Arctic plant-beds, which occur in a deep Drift-filled channel. The relative levels and stratigraphy point to the conclusion that the Hedge Lane deposits belong to a slightly earlier stage of the Low-Terrace River-drift than the deposits of Ponder's End. Broadly speaking, they undoubtedly belong to the same group.

The author suggests that it would be a practical convenience if the East Anglian word 'platymore' were adopted for the underlying eroded floor of country-rock beneath a later accumulation of drift. The importance of this 'platymore' surface in the correlation of Drift deposits has been increasingly recognized during recent years, and it seems desirable that it should have a name.

The author supports the correctness of the view that the lower river-terraces are later than the higher river-terraces. Further evidence is also brought forward in support of his view that the Arctic deposits form an integral part of the Low-Terrace Drift:

that is to say, that they belong to the latest stages in the Pleistocene erosion of the valley, and are not remnants of earlier deposits.

One of the sections described appears to suggest that the climate became nearly as temperate as that of the present day before the mammoth and woolly rhinoceros became extinct.

April 28th.—**Dr. A. Smith Woodward, F.R.S., President,** in the Chair.

The following communications were read :—

1. ' A Composite Gneiss near Barna in the County of Galway.' By Prof Grenville A. J. Cole, F.G.S., M.R.I.A., Director of the Geological Survey of Ireland.

The great mass of granite west of Galway town is seen on its northern margin to be intrusive in a metamorphosed series of Dalradian quartzites, limestones, and mica-schists, and has received a foliation which is parallel with the bedding of this series ; this foliation is ascribed by the author to the partial absorption of sheets of the bedded series into its mass. Traces of similar intermingling occur in Townparks (Galway town) and west of Barna. At Furbogh Bridge, the granite contains pink crystals of orthoclase, at times 10 cm. long in the direction of the vertical axis, and these have become stranded, as it were, among the foliation-planes of dark green biotite-schist, into which they were carried by an intimate intermingling of the granite with the schist into which it flowed. Quartz and smaller felspar-crystals from the granite abound in the resulting composite gneiss, and the general effect is comparable with that of igneous intermixtures described from County Down and Skye. In the Galway instance, however, there is no sign of general fusion of the invaded rock, which retains its original foliation and controls the structure of the composite mass.

2. ' Further Work on the Igneous Rocks associated with the Carboniferous Limestone of the Bristol District.' By Sidney Hugh Reynolds, M.A., Sc.D., F.G.S., Professor of Geology in the University of Bristol.

The paper gives an account of the additional information, concerning the Carboniferous volcanic rocks of North Somerset, which has become available, largely through digging trial-holes, since the publication in the Q. J. G. S. for 1904 (vol. lx) of a paper by Prof. Lloyd Morgan and the author on the subject. The rocks occur at five localities :—(1) Goblin Combe ; (2) Uphill ; (3) Limeridge Wood, Tickenham ; (4) Spring Cove and Milton Hill, Weston-super-Mare ; and (5) Woodspring or Middle Hope.

At Goblin Combe, as the result of digging nearly forty trial-holes, it was ascertained that the igneous rocks form two discontinuous, somewhat crescentic masses, each consisting of olivine-basalt overlain by a considerable thickness of calcareous tuff. At Uphill, the evidence obtained was insufficient to determine whether the basalt is a sill or a lava-flow. At Limeridge Wood, Tickenham, where only débris of basalt had previously been recorded, the presence of an oval mass measuring about 60 by 25 yards was proved by digging trial-holes, and the fact that it is completely surrounded by limestone indicates its intrusive character. Several additional exposures are described on Milton Hill, where the lava forms a band about 150 feet thick. The lava of Middle Hope or Woodspring is shown to form an irregular and discontinuous mass.

Previous statements as to the essentially basaltic character of these rocks are confirmed. Olivine is present at each locality. Analyses, mainly made by Mr. E. G. Radley, show that in some of the rocks a high percentage of potash is present.

June 9th.—Dr. A. Smith Woodward, F.R.S., President, in the Chair.

The following communications were read:—

1. 'The Accessory Minerals of the Granitic Rocks of the English Lake District.' By R. H. Rastall, M.A., F.G.S., and W. H. Wilcockson, B.A.

The work described in this paper arose out of independent researches on the mineral composition of sediments, in which it became desirable to study the genesis of certain minerals. Preliminary investigations promised results of interest if the rocks of a whole district were examined, and for this purpose the Lake District was selected. The rocks here described are the granites of Skiddaw, Shap, and Eskdale, the microgranite of Threlkeld, and the granophyre of Buttermere and Ennerdale.

The material was pounded in a mortar, washed and panned, and the concentrate separated in bromoform after the removal of the magnetic portion.

The general results showed a well-marked variation of accessory minerals between the different intrusions, but a similarity between parts of the same intrusion, although the minerals of apophyses are not always the same as those of the main mass. No evidence is afforded for a genetic connexion between the different intrusions.

One of the most remarkable results obtained is the rarity of magnetite and the wide prevalence of pyrrhotite, which was present in every sample examined, some thirty in number. Special attention was paid to the characteristics of the zircon-crystals, which

lent no support to the conclusions of Chrustchoff as to the occurrence of definite types in granite and gneissose rocks respectively. In parts of both the Skiddaw granite and the Threlkeld microgranite, anatase and brookite were found in abundance. It was not possible to determine their origin. Epidote is the characteristic mineral of the Ennerdale granophyre, while garnet is abundant at Threlkeld and Eskdale. The Eskdale granite also contains much tourmaline. The Shap granite is especially characterized by apatite and sphene.

It is concluded that descriptions of accessory minerals founded only on examination of rock-slices are inadequate and misleading; it is only by concentration that the rarer constituents can be satisfactorily determined.

2. 'The Rocks of the Lyd Valley, above Lydford (Dartmoor).' By Frederic Philip Mennell, F.G.S.

The paper deals chiefly with a small area on the north-east of Dartmoor, though some of the conclusions are applicable to nearly all that part of the moor which lies north of the portion recently mapped by the Geological Survey. In the immediate neighbourhood of Lydford the progressive alteration of the Carboniferous rocks within the metamorphic aureole surrounding the granite is described in detail, and it is shown that they are consistently cordierite- and biotite-bearing, like those examined by Mr. Barrow at Holne. North of the altered limestone or 'calc-flinta' of Downtown, however, the type of alteration is entirely different, and leads to the inference that the beds are quite distinct. The change is of much more than local significance, as from this point all round the north of the moor, at least as far as South Zeal, there is no bed of any thickness containing cordierite, while chiastolite, white mica, and andalusite proper, are characteristic. Coarse andalusite-rock and altered shale, with remarkable skeleton-crystals of chiastolite, are described from the Nodden quarries, together with other types of hornfels. It is clear that the beds occupying the northern part of the contact-zone belong to a definite series. There is strong evidence that the cover of the granite mass has a dome-like character, and that precisely the same stratigraphical horizon is in immediate contact with the granite all the way from Sourton to Drewsteignton.

The granite of Brator, not far from the best exposures of coarse cordierite-hornfels, is described. It is a biotite-bearing rock containing a little microcline, as well as orthoclase and oligoclase. It is rich in cordierite, recrystallized from sedimentary material absorbed into the magma. Several offshoots from the granite have been noted at various points along the Lyd. One near Nodden Gate is of interest, as containing topaz in remarkable abundance.

L. *Light Absorption and Fluorescence.—*IV. *Change in Absorption with Concentration.* By E. C. C. BALY, *M.Sc., F.R.S., Grant Professor of Inorganic Chemistry in the University of Liverpool, and* F. G. TRYHORN, *M.Sc.*[*]

IN the previous papers of this series the relation between the frequencies of the absorption and fluorescence bands in the ultra-violet and infra-red regions has been dealt with [†]. Since the absorption spectra of the majority of compounds can only be observed when they are in solution, it becomes necessary to discuss the changes in absorption that are produced by the solvent in order to determine whether the relationships established for the vapour spectra of substances are perfectly general. In the present paper it is proposed to deal with the change in the position of an absorption band and the change in absorptive power produced by a solvent, and to show how such variations are due to the nature of the solvent and to the concentration.

In the first place, the change in the position of the absorption band with concentration may be dealt with. In Table I. are given the positions of the centre of the absorption band of pyridine solutions at given concentrations, the solvent being CO_2-free water. In the first column are given the volumes in litres in which one gram-molecule of pyridine (79 grams) is dissolved, while the second and third columns

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contain the wave-lengths and wave-numbers respectively of the centre of the absorption band.

Table I.

V.	λ.	1/λ.	Factors.	Infra-red Band.
·08065	2580	3876	$12 \times 323 \cdot 0$	$3 \cdot 096 \, \mu$
0·1	2612	3828	$12 \times 319 \cdot 0$	$3 \cdot 135$
0·160	2595	3853	$12 \times 321 \cdot 1$	$3 \cdot 114$
10·0	2572	3888	$12 \times 324 \cdot 00$	$3 \cdot 086$
12·0	2570	3891	$12 \times 324 \cdot 25$	$3 \cdot 084$
500	2562	3903	$12 \times 325 \cdot 25$	$3 \cdot 075$
25000	2558	3910	$12 \times 325 \cdot 83$	$3 \cdot 069$

The first value (V = 0·08065) refers to pure liquid pyridine, and, as can be seen, the band shifts towards the red on the addition of a small quantity of solvent and then back towards the ultra-violet as the concentration of the solution decreases. It is obvious from the values given in the table that the wave-number of the centre of the band at infinite dilution must be a little greater than $1/\lambda = 3910$. Now the absorption of the vapour of pyridine has been observed by Purvis [*], who has measured the wave-lengths of fifty-three absorption lines composing the single band group. The wave-numbers of these may be arranged symmetrically around the strong line with wave-length $\lambda = 2789$ as centre. Then, as shown in the previous paper [†], the differences between the wave-numbers of the central line and the wave-numbers of the other lines must equal the wave-numbers of the infra-red bands of pyridine. As the infra-red spectrum of pyridine has only been observed between the limits $3 \, \mu$ and $13 \, \mu$, it is only possible to determine whether the relation holds good between these limits. It is, however, manifest that the relation holds good from the values given in Table II. The first and second columns contain the wave-lengths of the absorption lines as measured by Purvis and their wave-numbers $(1/\lambda)$. The third column shows the wave-number differences between each line and the central line; while the fourth column contains the means of the two values where such exist. The reciprocals of these differences or the wave-lengths of these infra-red bands are given in the fifth column.

[*] Trans. Chem. Soc. xcvii. p. 692 (1910).
[†] Phil. Mag. xxix. p. 223 (1915).

In the sixth and seventh columns are shown the wave-lengths of the infra-red bands as observed by Coblentz [*] and by Spence [†].

Table II.

λ.	1/λ.	ν_{r}.	Mean ν_{r}.	Infra-red Bands.		
				Calc.	Obs. Coblentz.	Obs. Spence.
2930	3413	174	...	5·75 μ	5·80 μ	
2918	3427	160	...	6·25	6·25	6·35 μ
2908	3439	148	147·5	6·79	6·75	
2892	3458	129	129·5	7·72	7·75	
2879	3473·5	113·5	...	8·81	8·78	8·80
2872	3482	105	...	9·52	9·35	9·50
2869	3486	101	...	9·90	9·73	9·77
2866	3489	98	98·75	10·13	10·08	10·15
2861	3495	92	92	10·87	10·85	
2860	3497	90	...	11·11	11·28	
2855	3503	84	84	11·90	11·90	
2789	3587	0				
2730	3663	76	...	13·16	13·3	
2726	3668	81	...	12·35	12·4	
2724	3671	84	84	11·90	11·90	
2718	3679	92	92	10·87	10·85	
2712·5	3686·5	99·5	98·75	10·13	10·08	10·15
2696	3709	122	...	10·32	10·53	
2690	3717	130	129·5	7·72	7·75	
2685	3724	137	...	7·30	7·30	
2681	3730	143	...	6·97	6·95	6·95
2678	3734	147	147·5	6·79	6·75	

It may be seen that the agreement between the calculated and observed values is exceedingly good. It is an interesting fact that the absorption-band group as observed for pyridine vapour is not the same as for that observed with a solution of pyridine, for the centre of the former is at $1/\lambda = 3587$, while the centre of the latter in dilute solution, as shown in Table I., is about $1/\lambda = 3910$. This fact has already been noted by Purvis, and is of some value in the present connexion because it enables us to determine whether the relation between the wave-numbers of the centres of two absorption-band groups holds good. Now the difference between the above values of $1/\lambda$ for the two absorption bands is 323, and therefore this must be very nearly the fundamental infra-red wave-number of pyridine.

Since the value of $1/\lambda = 3587$ may be taken as an

accurate measurement of the central wave-number of the
less refrangible ultra-violet band, and since, further, this
must be an exact multiple of the true fundamental wave-
number, it follows that the true fundamental wave-number
must be $\frac{3587}{11} = 326 \cdot 09$, because 11 is the only integral
divisor which gives a value a little larger than 323. It
follows, therefore, that the wave-number of the fundamental
infra-red band of pyridine vapour should be $1/326 \cdot 09 =$
$3 \cdot 066 \mu$, and also that the central wave-number of the more
refrangible pyridine vapour band should be $12 \times 326 \cdot 09 =$
$3913 \cdot 08$. As was pointed out above, the values given in
Table I. show that the central wave-number of the absorption
band at infinite dilution is a little greater than 3910, and it
is therefore evident that with increasing dilution the centre
of the absorption band approaches the true value for the
vapour. The measurements in Table I. show that the
maximum shift occurs in 10 N solution, which almost exactly
corresponds to the molecular ratio of C_5H_5N to H_2O of $1:1$;
and therefore it may be concluded that the maximum effect
of the water, as far as altering the free vibration period of
pyridine is concerned, occurs when the solvent and solute
are in the proportions agreeing with the monohydrate
C_5H_5N, H_2O, and that the influence of the water decreases
with dilution until, finally, the free vibration period becomes
the same as that of pyridine vapour.

It is also evident that we now have an explanation of the
variation in position of an absorption band when a substance
is examined in solution, namely, that it is due to a combina-
tion or a tendency to a combination of the substance with
the solvent. Moreover, it also follows that the fundamental
infra-red band must also shift with solution; and in the
fourth column of Table I. are given the wave-numbers of
this infra-red band at the various dilutions, *i. e.* $1/\lambda \div 12$.
The wave-lengths of the infra-red bands are given in the
fifth column of Table I. For obvious reasons it is impos-
sible to measure the infra-red band for dilute solutions, but
from some observations made in these laboratories it is clear
that this band shifts in a manner comparable with that shown
in Table I. The wave-numbers of the infra-red band have
been plotted against the logarithms of the corresponding
volumes of solution, and the curve obtained is shown in
fig. 1, curve I.

From the value given in Table I. it is clear that the
fundamental infra-red band of pure homogeneous liquid
pyridine should lie at $3 \cdot 096 \mu$. The absorption at this

region of the spectrum of pyridine is somewhat complex owing to the bands at $2\cdot95\,\mu$ and $3\cdot25\,\mu$, due to the nitrogen atom and the hydrocarbon chain respectively. The first and second harmonics of the fundamental band for a thin film of liquid pyridine have, however, clearly been observed by Coblentz at $6\cdot25\,\mu$ and $9\cdot35\,\mu$ and by Spence at $6\cdot35\,\mu$ and $9\cdot50\,\mu$.

We have also examined the less refrangible band of salicylaldehyde, and the values obtained are shown in Table III., the solvent in this case being alcohol.

TABLE III.

V.	$1/\lambda$.	Factors.	Infra-red Band.
0·1042	3084	$19\times162\cdot35$	$6\cdot16\,\mu$
0·208	3074	$19\times161\cdot8$	6·18
1	3059	19×161	6·21
10	3045	$19\times160\cdot27$	6·24
16	3040	19×160	6·25
20	3039	$19\times159\cdot9$	6·254
320	3049	$19\times160\cdot4$	6·23
1280	3066	$19\times161\cdot4$	6·20
50000	3101	$19\times163\cdot2$	6·13

It was not found possible to examine solutions of less concentration than $V=50,000$ owing to the limitations set by the spectrophotometer, but it is obvious that the limiting value of $1/\lambda$ is greater than 3101. Now Purvis [*] has measured the wave-lengths of the component lines of the more refrangible band of salicylaldehyde vapour, and there is no doubt that the central line in this case is at $\lambda=2514$ or $1/\lambda=3978$. On the other hand, the infra-red spectrum of salicylaldehyde has not been observed, and therefore we can gain no direct information as regards the value of the fundamental wave-number in this region.

It is, however, clear from analogy with other compounds, since $1/\lambda=3978$ is the central line of one absorption band of salicylaldehyde vapour, that, if ν_x be the fundamental infra-red wave-number, $x\nu_x$ must equal 3978 and $y\nu_x$ must equal some number which is rather larger than 3101, x and y being two integers. We have observed both absorption bands of the aldehyde in alcoholic solution when $V=1280$,

* Trans. Chem. Soc. cv. p. 2482 (1914).

and the centres of the two bands are then at $1/\lambda = 3066$ and
3874 respectively.   In this case, since the concentration is
the same for both bands, it is obvious that

$$\frac{3066}{y} = \frac{3874}{x} = \text{the wave-number of the infra-red band}$$
at the concentration $V = 1280$.
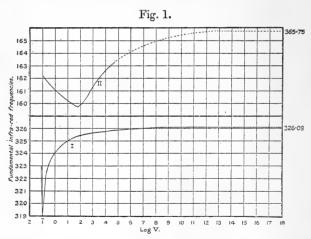
Since x and y are two integers the only possible solution is

$$\frac{3066}{19} = \frac{3874}{24} = 161\cdot4.$$

It follows that the wave-number of the less refrangible band
in alcoholic solution is $19 \times \nu_x$, and that the wave-number of
the more refrangible band is $24 \times \nu_x$.   The true value of
ν_x for salicylaldehyde vapour must therefore be

$$\frac{3978}{24} = 165\cdot75.$$

In the third and fourth columns of Table III. are given
the wave-numbers of the infra-red band and the corre-
sponding wave-lengths calculated on the basis $y = 19$.   In
fig. 1, curve II. is shown the relation between ν_x and the

Fig. 1.

concentration from the values given in Table III.   The
dotted portion of the curve is extrapolated to show that by
analogy with the corresponding pyridine curve, the calcu-
lated value of $165\cdot75$ is very probably correct.   The general
conclusions, therefore, drawn from pyridine are thus fully
confirmed by salicylaldehyde, namely, that on the addition
of a solvent the absorption band first shifts towards the red,

and then on further dilution it shifts towards the shorter wave-lengths, until it finally reaches the true value for the vapour.

One further example may be given, namely, that of aniline, which is interesting from the fact that it shows two absorption-band groups in alcoholic solution. The central wave-numbers of these two bands have been measured at very great dilution ($V = 84,000$) and were found to be 3496·7 and 4255 respectively. Now these two wave-numbers must be even multiples of the fundamental infra-red wave-number, and therefore we have

$$\frac{3496 \cdot 7}{x} = \frac{4255}{y} = \nu_x,$$

where ν_x is the true fundamental infra-red frequency of aniline and x and y are whole numbers. The only solution is given by $x = 23$ and $y = 28$, whence the true values of ν_x are found to be 152·03 and 151·97 respectively. Now Purvis [*] has observed the less refrangible absorption band of aniline vapour, and from his measurements it is clear that the central wave-number is $1/\lambda = 3496 \cdot 1$. As this value is obviously more accurate than that obtained from the solution, we may take the true value of ν_x for aniline to be $3496 \cdot 1/23 = 152$, which is a mean of the two solution values. It follows, therefore, that aniline vapour should show a very strong absorption band at $1/152 = 6 \cdot 58\,\mu$, or at the first multiple of this, $3 \cdot 29\,\mu$. The absorption of a liquid film of aniline has been observed by Coblentz [†], and in comparing the absorption spectra of vapour and liquid it must be remembered that in the latter the bands will have slightly longer wave-lengths. The value obtained by Coblentz was $3 \cdot 34\,\mu$ instead of $3 \cdot 29\,\mu$.

These results are of some importance, for, in the first place, they show that the relationship between the infra-red and ultra-violet absorption bands pointed out in the previous papers, namely that the central wave-numbers of the latter are whole multiples of a fundamental wave-number in the infra-red, holds good in solution. In the second place, they would seem to offer an explanation of the well-known fact that in general there is a shift in the position of an absorption band when the substance is dissolved in a solvent. Since the central wave-number is a whole multiple of a fundamental infra-red wave-number, the shift must be due to the fact that the fundamental wave-number changes on

* Trans. Chem. Soc. xcvii. p. 1546 (1910).
† *Loc. cit.*

solution, and it may be noted that a small change in this fundamental wave-number will produce a relatively larger shift in those wave-numbers which are its multiples. Although we have observed that the fundamental infra-red band shifts on solution by an amount and in the direction comparable to that of its multiples, yet no accurate observations of the infra-red absorption spectra of substances in solution have been published. We have examined the absorption spectrum of an alcoholic solution of β-naphthol ethyl ether in the neighbourhood of $3\,\mu$, where both solvent and solute each show strong absorption bands. We found, however, that the two types of molecules do not separately exhibit their own absorption bands, but that the solution shows only one absorption band, which moreover is not a mean of the two due to the two components. The solution absorbs as if it were a single entity with an absorption band of its own which differs from that of each component.

It is possible that this will explain the interesting fact that the wave-length of the infra-red emission band of the Bunsen flame is not the same as that of either carbon monoxide or carbon dioxide. On the other hand, the two oxides are in equilibrium in the flame, and it is this equilibrium which is emitting the radiation. Just as a solution seems to exhibit an absorption band of its own and not the bands peculiar to its components, so the equilibrium of carbon monoxide and carbon dioxide present in the Bunsen flame emits a radiation of its own and not that of its components.

We thus arrive at a reasonable explanation of the change in position of absorption bands when the absorbing substance is dissolved in a solvent, namely, that the solution acts as a single entity with its own fundamental frequency of vibration in the infra-red. Since the frequencies of the absorption bands in the visible and ultra-violet regions are multiples of this fundamental frequency, we see that these must shift in the presence of a solvent.

As has been pointed out in the previous papers of this series, one of the results of the relationship between the fundamental infra-red frequency and the phosphorescent, fluorescent, and absorption bands in the visible and ultra-violet regions, is the existence of constant differences between the wave-numbers of the latter. Since the relationship can obviously only hold good when all the wave-numbers are characteristic of one molecular entity, the constant differences may be taken as evidence of the presence of one molecular entity. The existence of the constant differences enables us

to be independent of a knowledge of the infra-red spectrum, a matter of great importance in view of the fact that the infra-red absorption spectra have been observed of only relatively few substances. This is partly due to the fact that the experimental technique is relatively difficult, but also to the fact that no investigations have been made of the absorption of solutions in the infra-red region. The result has been that solids of high melting-point have not been examined. In view of what was said above about solutions, it is to be hoped that investigations of their infra-red absorption will be undertaken, and, indeed, we ourselves look forward, when more pressing matters have been disposed of, to carrying out some of the work in this field.

In the absence of knowledge of the infra-red spectra, it is possible, as stated above, to argue from the constant wave-number differences between the bands in the visible and ultra-violet regions. The existence of these constant differences has now been proved for so many compounds, that the relationship may finally be accepted as absolute. It therefore becomes possible to use the converse argument, namely that, if a substance exhibits different absorption bands in different solvents and if the constant difference relation holds good between the various absorption bands, the change in absorption in passing from one solvent to another cannot be interpreted as an indication that the substance has changed its constitution. It is, however, believed by many chemists that a change in absorption produced by a change in solvent always means a change in the primary structure of the compound in the chemical sense, the belief being apparently based upon the conception that a particular absorption curve must be characteristic of a definite molecular structure, and that it is not possible to call into play any free period of vibration which previously was latent. As may readily be understood, it was not possible to prove the existence of the constant difference relation for solutions until the variation in the position of the absorption bands with concentration had been worked out. Now that this variation is understood, it is possible to apply the argument to the problems of chemical constitution. This has now been done for the phenols and nitrophenols with results that are eminently satisfactory, but a description of this work must be reserved for a further paper.

The second point to be discussed is the variation in the absorptive power with concentration of the absorbing compound in a given solvent.

According to the well-known law the absorptive power is expressed by the relation

$$\frac{I_0}{I} = e^{kdc},$$

where I_0 and I are the intensities of the incident and emergent light respectively, d the thickness of the absorbing layer, c the concentration, and k the absorption constant. In actual experiment the absorption is best expressed in terms of that exerted by 1 cm. of a molar solution (one molecular weight dissolved in one litre of solution). The value of k, which according to Beer's law should be constant, is readily enough found from

$$\log\frac{I_0}{I}\Big/\lambda dc = k.$$

In practice, however, it is rarely found that Beer's law holds good, but up to the present no expression has been found which connects the value of k with the concentration. Some previous observations of the absorptive power of aqueous solutions of pyridine * have shown qualitatively that it increases very materially as the concentration decreases. An interesting fact in connexion with pyridine is that its absorptive power is much greater in acid solution than in neutral solvents †. This at once affords a considerable range of solvents, and we have determined quantitatively the value of k for pyridine solutions in the following solvents—water, alcohol, N/5000 aqueous hydrochloric acid, N/1 aqueous hydrochloric acid, and concentrated sulphuric acid. In the case of the neutral solvents, considerable care was necessary to guard against the absorption of atmospheric carbon dioxide which at once gave too high values for k. In the case of each solvent, the absorptive power of pyridine increases rapidly with the dilution until a constant value is reached, and the values observed are given in Table IV.

In previous papers ‡ the view has been put forward that the molecules of every substance are surrounded by a more or less condensed force field of electromagnetic type. These fields are opened or unlocked by the influence of a solvent, such opening up taking place in definite stages. Each of

* Baly and Rice, Trans. Chem. Soc. ciii. p. 91 (1913).
† Hartley, *ibid.* xlvii. p. 685 (1885), and Baker and Baly, *ibid,* xci. p. 1122 (1907).
‡ Baly and Krulla, Trans. Chem. Soc. ci. p. 1469 (1912); Baly and Rice, *ibid.* ci. p. 1475 (1912), ciii. pp. 91 & 2085 (1913); and Baly, Phil. Mag. xxvii. p. 632 (1914), xxix. p. 223 (1915).

these stages is characterized by its power of absorbing light rays of definite wave-length, and consequently when only one absorption band is shown, as in the case of pyridine, only one stage in the opening up is present, and we are therefore only concerned with the equilibrium between the closed fields and the fields when opened up to one only of the possible stages. It is obvious, from the fact that the absorptive power increases with dilution, that the solvent increases the amount of the opened up stage present. The mass-action law as usually conceived does not therefore hold good, since if b is the fraction of the molecules opened up, the mass-action law leads to the relation $\dfrac{b}{1-b} =$ constant. In other words, the fraction opened up, and therefore k, should be independent of the concentration. On the other hand, an increase in the mass of the solvent increases the relative number of opened-up molecules in the equilibrium up to a constant value when the solvent has opened up the maximum possible for that solvent. If f be the fraction of that maximum which exists at any given concentration, it is clear that f must lie between 0 at $V = 0$ (infinitely large concentration) and 1 at $V = \infty$ (infinitely small concentration), and, further, that f is some function of the concentration. The simplest possible relation connecting f with the mass of the solvent under the given conditions

$$f = 1 - e^{-\alpha V},$$

where α is a constant characteristic of the substance and the solvent used. It is a justifiable assumption to make that the absorptive power (k) is proportional to the concentration of the opened up stage, and we may therefore put

$$f = \frac{k}{K},$$

where K is the maximum and constant value of k in the given solvent. We thus have

$$\frac{k}{K} = 1 - e^{-\alpha V},$$

whence
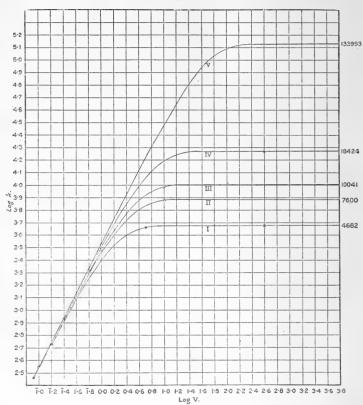
$$\frac{K - k}{K} = e^{-\alpha V},$$

and

$$\log \frac{K}{K - k} = \alpha V.$$

From this formula the absorptive power of pyridine at various concentrations in the five different solvents has been calculated, and the curves showing the relation between k and V are given in fig. 2. For convenience in plotting the

Fig. 2.

Absorptive power of pyridine.

Curve   I in water.   Curve IV in N/1 HCl.
   ,,   II in alcohol.   ,,   V in concentrated H_2SO_4.
   ,,   III in N/5000 HCl.

logarithms of k have been placed on the ordinates and the logarithms of V on the abscissæ. The crosses on the curves are the values experimentally found and shown in Table IV. As may be seen, these experimental values lie on the appropriate curve in every instance. The values of α were calculated from the absorptive power of pure pyridine and the

TABLE IV.—Absorptive Power (k) of Pyridine in Various Solvents calculated from the formula

$$\frac{k}{K} = 1 - e^{-aV}.$$

V.	Water. Calc.	Water. Obs.	Alcohol. Calc.	Alcohol. Obs.	N/5000 HCl. Calc.	N/5000 HCl. Obs.	N/1 HCl. Calc.	N/1 HCl. Obs.	Conc. H₂SO₄. Calc.	Conc. H₂SO₄. Obs.
0·08065	285·6	285·6	285·6	285·6	285·6	285·6	285·6	285·6	285·6	285·6
0·1	351·5	356	352·5		352·9		353		354	
0·160	549·5	550	555·9		558·5		562		566	
0·2	676·6		688·5		693·2		700		706	
0·3	977·2		1009		1022		1040		1059	
0·4	1255		1315		1339		1373		1401	
0·6	1750		1884		1940		2021		2110	
1·0	2536	2500	2873	2880	3020	2990	3243	3260	3499	3521
2·0	3699		4660		5313		5915		6906	
4·0	4475		6462		7640		9930		13457	
5·0	4587		6892		8362		11425		16604	
6·0	4639		7160		8865		12657		19669	
10·0	4680	4600	7534	7510	9760	9750	15765		31150	
20·0							18040		55060	
40·0							18416		87494	
60·0					10033		18423		106601	
100·0									124487	
200·0			7599						133926	
400·0	4682	4682							133990	
2000·0			7600						133990	
32000·0				7600	10041	10041	18424	18424	133993	133993
80000·0				7600	10041	10041	18424	18424	133993	133993

Values of a:—Water, 0·33889; Alcohol, 0·20621; N/5000 HCl, 0·15537; N/1 HCl, 0·04072; Concentrated H₂SO₄, 0·11491.

appropriate K only, and hence the agreement between observation and calculation is eminently satisfactory [*].

It would seem possible that with suitable modifications the formula

$$f = 1 - e^{-a\mathbf{V}}$$

might find a more general application to solution phenomena, for in such cases as the dissociation of strong electrolytes the mass-action law again does not hold. In its present form the expression only deals with the simplest case of one molecular entity changing into another molecular entity. If, for example, the solvent convert one molecule into two entities, *e. g.* ions, then the effective concentration of the new entities will be proportional to $\sqrt{V}$, and we shall have

$$f = 1 - e^{-a\sqrt{\mathbf{V}}}.$$

If for f be put λ/λ_0, where λ and λ_0 are the molecular conductivities of a solution of concentration V and at infinite dilution respectively, then

$$\log\frac{\lambda_0}{\lambda_0 - \lambda} = a\sqrt{\overline{\mathbf{V}}}.$$

This formula is found to express the molecular conductivities of weak electrolytes with absolute accuracy at concentrations smaller than $V = 4$, and of strong electrolytes also over a fair range of concentration. A discussion of this cannot be given here, but the matter is mentioned in order to show that the formula may find considerable application to solution phenomena.

The University, Liverpool.

LI. *On the Energy of the Secondary Beta Rays produced by Partly-absorbed Gamma Rays.* By H. F. BIGGS, *B.A., Assistant Lecturer in Mathematics in the University of Manchester*[†].

Object and Results of the Experiment.

RUTHERFORD [‡] has brought forward strong evidence to show that the β particles which give the lines of the magnetic spectrum of the β radiation from RaB and RaC carry energy in whole multiples of the quanta corresponding

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    † Communicated by Sir E. Rutherford, F.R.S.
    ‡ Rutherford, Phil. Mag. xxviii. p. 305 (1914).

to the frequencies that Rutherford and Andrade* found for the γ rays of RaB and RaC respectively. Further, Rutherford, Robinson, and Rawlinson †, by using an emanation-tube wrapped in lead foil, obtained the magnetic spectrum of secondary β rays produced from lead by the γ rays of RaB and RaC, and found that all the observable lines were nearly, if not quite, identical with the primary β-ray lines of RaB. Lines corresponding to the faster primary β rays of RaC were probably also present, but were difficult to observe with certainty owing to their relative faintness and the fogging from scattered radiation in this region of the plate. It is thus indicated that the secondary β rays produced from lead by the γ rays have a spectrum identical, or nearly so, with that of the primary β rays. and therefore, like the latter, derive their energy in quanta from the γ rays.

The question then arises whether the number of quanta which γ rays of given frequency may impart to secondary β particles is independent of the energy of the impinging γ rays, or whether the γ rays, when they lose energy in passing through matter, may lose also the power of producing β rays of great energy—whether, for instance, γ rays that originally can impart energy $5h\nu$ to an electron may be able, after passing through a centimetre of lead, to impart at most the energy $3h\nu$. For it seems probable that in passing through matter γ rays may lose energy in some other way than by the production of β rays. Thus the scattering of γ rays investigated by Florance‡ may be due to the forced vibration of electrons that remain in the atom, and therefore absorb less energy than those projected as secondary β rays. If this is so, we should expect that the γ rays, after passing through a considerable thickness of matter, would be, as it were, shorn of some of their available quanta, and that therefore their secondary β radiation would be, on the whole, less penetrating than that of the unaffected γ rays.

It was to investigate this point that Sir Ernest Rutherford suggested the present research, which is a modification of a research carried out by Eve § in 1904.

It was found that if this effect of matter on the γ rays exists, it lies beyond the range of the method used.

* Rutherford and Andrade, Phil. Mag. xxvii. p. 854 (1914); Phil. Mag. xxviii. p. 263 (1914).

† Rutherford, Robinson, and Rawlinson, Phil. Mag. xxviii. p. 281 (1914).
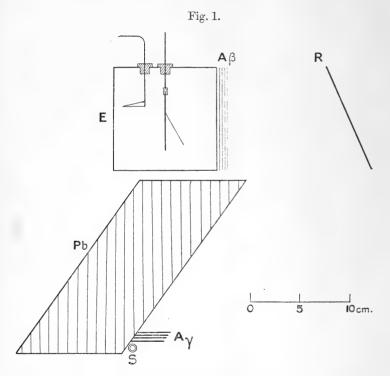
‡ Florance, Phil. Mag. xxvii. p. 225 (1914).

§ Eve, Phil. Mag. viii. p. 669 (1904).

Incidentally, the results confirm Rutherford's theory that the observed great energy of the faster β particles is derived from the known γ rays, each β particle carrying *several* of their energy quanta, and is not due to a hypothetical γ radiation of such high frequency that only *one* quantum of energy is required.

Apparatus.

The source, S (fig. 1), of γ rays was 64 mg. of $RaBr_2$ with its products in a steady state. The radium was contained

Fig. 1.

in a platinum tube enclosed in a sealed glass tube. The glass tube was fixed to a lead plate so that it could be removed (for safe keeping) and exactly replaced. Pb is a lead block so placed that the shortest line from any radium to the nearest point of the electroscope lay through about 20 cm. of lead. The electroscope, E, 10 cm. cube, was of block tin with a lead casing 3 mm. thick. One side was closed only by aluminium foil. Opposite this side could be hung on a light frame the radiator, R, a piece of lead foil 10 cm. square

and ·12 mm. thick. Absorbing screens Aβ could be placed over the side of the electroscope, and other screens, Aγ, directly over the source.

Method.

Series of observations were taken of the ionization in the electroscope both with the radiator in place and with the radiator removed. The ionization due to the secondary radiation from the radiator is then obtained by subtraction of the smoothed curves.

Two methods of arranging the observations were used. In the first, a series of absorption curves for the secondary β rays was taken, the different curves corresponding to different thicknesses of matter traversed by the primary γ rays. Each curve shows the ionization plotted against the thickness of aluminium in the screen Aβ which absorbs the secondary radiation. Any marked change in the energy-distribution of the secondary radiation should then be made apparent in a change of shape of the curve as we pass down the series.

Fig. 2.
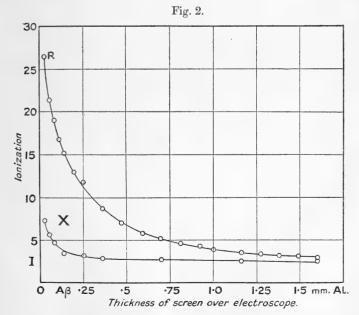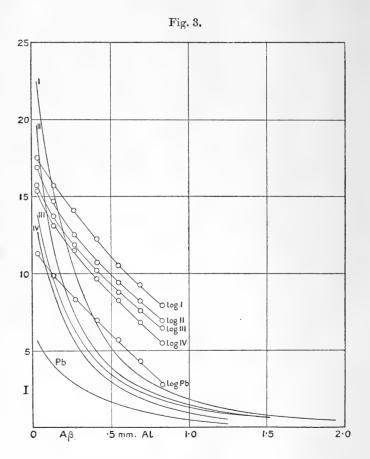
Fig. 2 shows a pair of experimental curves typical of these observations, that is, ionization (in arbitrary units)

plotted against the thickness (in millimetres) of aluminium through which the secondary rays have passed. The screen Aγ over the source is, in this case, ·76 cm. of aluminium. Curve R is for the radiator in place, curve X for the radiator removed.

Fig. 3 gives (in curve ii.) the result of subtracting curve X from curve R in fig. 2, using the smoothed curves, with the

Fig. 3.

other curves of the same type; that is, curves i., ii., iii., iv., Pb, are absorption curves in aluminium for the secondary radiation due to primary radiation that has passed through 0, ·76, 1·52, 2·28 cm. of aluminium, and 1·71 cm. of lead respectively,

together with the platinum and glass of the tubes enclosing the source. To facilitate comparison, the logarithms of the ordinates are also plotted. The curves thus obtained would, of course, be identical if the energy-*distribution* of the secondary β rays were independent of the thickness of matter passed through by the γ rays. The observed differences between the curves may be accounted for by the relative weakening of the softer primary γ rays. In fact, the curves form a series very much like what would be expected if the β rays produced by γ rays of given frequency had always the same velocity, or velocities, *i. e.* if the energy-distribution of the secondary β rays due to any one frequency of γ rays were independent of the energy of those γ rays.

In the second method, the screen Aβ over the electroscope is kept constant for each curve, while the screen Aγ over the source is varied. Thus the ionization produced by β rays that have traversed the same matter is plotted against the thickness of matter traversed by the primary γ rays that produce these β rays.
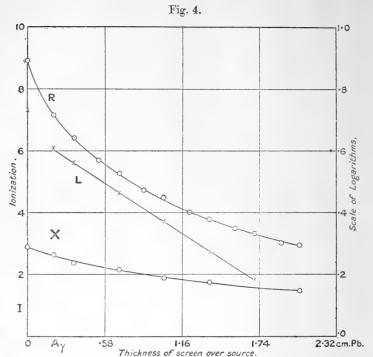
This procedure should show up at once any change in the maximum energy of the secondary β rays when the primary γ rays pass through matter; for, if we consider the case where the electroscope-screen is so thick that only the faster β rays get through when the γ rays are unscreened, it is obvious that a fall in the maximum energy of the secondary β rays will be shown as a sudden drop in the curve. Ideally, of course, the same curves might have been obtained by comparing the ordinates of curves such as those in fig. 3, but a glance at fig. 3 will show that the irregularities of scale make it preferable to obtain consecutive readings in the way mentioned.

It should be noticed that this method is only a variation of the ordinary experiment on the absorption of γ rays, for there also the γ rays are probably measured only by the ionization produced by the secondary β rays. The essential difference is merely that in the present experiment the secondary β rays are controlled, being made to pass through known thicknesses of matter before producing ionization. We should therefore expect the exponential law to hold as in the direct experiments; also, since the softer β rays are cut out, the effect of the softer γ rays that produce them should be less apparent, and therefore the exponential law would begin to hold for smaller thicknesses of screen absorbing the γ rays. Such turns out to be the case.

Fig. 4 gives a typical pair of curves obtained by this method.

Fig. 4.

Thickness of screen over source.

As before, curve R is for the radiator in place, curve X for the radiator removed. Curve L is obtained by plotting the logarithm of the difference of curves R and X. It is seen that the exponential law holds for thicknesses above 0·2 cm. of lead.

Fig. 4 shows the results for varying $A\gamma$, the screen over the source, when $A\beta$, the screen over the electroscope, is kept at ·47 mm. of aluminium. Similar results were obtained for $A\beta = ·25$ mm. and $A\beta = ·86$ mm. aluminium.

The following table—

$A\beta$, mm. Al.	Limits of x, cm. Pb.		μ, cm.$^{-1}$
·25	·6,	2·3	·64
·47	·3,	1·2	·66
·86	·4,	1·2	·67

gives the absorption coefficients, μ, of the γ rays in lead as measured by the falling-off of the ionization due to the secondary β rays projected from the lead radiator, which ionization follows the law $I = Ce^{-\mu x}$, where x cm. is the distance the γ rays travel through lead. The first column gives the thickness in millimetres of the aluminium screen, $A\beta$, over the electroscope through which the secondary β rays pass. The second column gives the range of x from the point where the logarithm-graph becomes straight to the point where measurements cease to be reliable.

It will be noticed that the values of μ agree well among themselves, and also agree roughly with that found directly by Rutherford and Richardson * and by Richardson † for the hardest γ rays of RaC.

The most important deduction to be made from this result is that there is no trace of γ rays more penetrating than those whose absorption-coefficients and frequencies are already known, even in the production of the hardest β rays. Indeed, the values obtained for μ may be said to amount to a proof that a secondary β particle derives its energy, not from γ radiation whose frequency is so great that *one* quantum suffices to account for this energy, but from γ rays of considerably lower frequency, which must therefore impart *several* of their quanta to each β particle. For instance, if we consider the β rays that pass through ·86 mm. of aluminium, which are produced by γ rays having an absorption-coefficient, $\mu = ·67$ cm.$^{-1}$ in lead, we find, using Varder's ‡ results, that these β rays must have energy at least equal to $6·2 \times 10^{13}e$, where e is the charge of an electron in electromagnetic units ; again, the absorption-coefficient ·67 cm.$^{-1}$ in lead corresponds to a frequency for which $h\nu = 1·2 \times 10^{13}e$. This number is deduced by Bragg's law, $\nu \propto \mu^{-2/5}$, from the absorption-coefficient in lead, $1·5$ cm.$^{-1}$, ascribed with much probability by Rutherford § to the γ rays of RaB whose wave-length is $1·37 \times 10^{-9}$. Thus no less than 5 quanta are needed to account for the energy of these β rays.

It should also be remarked that the results support Rutherford's conclusion that the preponderance of the harder β radiation is due to a single γ radiation. This is shown by the fact that the exponential law begins to hold good for smaller thicknesses of lead than when the absorption

* Rutherford and H. Richardson, Phil. Mag. xxv. p. 722 (1913).
† H. Richardson, Roy. Soc. Proc. A. xci. p. 398 (1915).
‡ Varder, Phil. Mag. xxix. p. 725 (1915).
§ Rutherford, Phil. Mag. xxx. p. 356 (1915).

curve of the γ rays is obtained directly. Again, if the divergence between the value here obtained for μ (·66 cm.$^{-1}$) and that found by Rutherford and by Richardson (·50 cm.$^{-1}$) is a genuine one, this is further evidence that the hard β rays are mainly due, not to the hardest γ rays reflected at 43′ from rock-salt, but to those reflected at 1° 0′.

There are two possible disturbing factors to be reckoned with, primary β rays producing secondary or scattered β rays, and secondary (scattered) γ rays from the radiator. The former, however, must be almost negligible, even for no extra screen Aγ, since the primary radiation has already passed through the platinum and glass in which the radium is contained. In fact, the curves themselves show that the primary β rays have been already almost totally absorbed. The effect of the secondary γ rays, on the other hand, is by no means negligible, though that it is small compared with that of the β rays is shown by the closeness with which the curves of fig. 3 approach to zero. We may, in fact, safely assume that the values found for μ really represent the falling-off of the secondary β radiation.
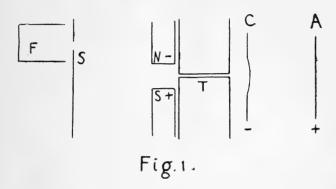
I wish to thank Sir Ernest Rutherford for suggesting this research and for the kind interest which he took in it while work was in progress.

LII. *The Ionization and Dissociation of Hydrogen Molecules and the Formation of H_3. By* A. J. Dempster, *late* 1851 *Exhibition Scholar of the University of Toronto* *.

BY the analysis of positive rays, J. J. Thomson has shown that in a discharge-tube containing hydrogen there are present charged atoms, charged molecules, and sometimes a constituent with a mass three times that of the atom of hydrogen. The pressure used was about ·003 mm. of mercury, and consequently the potential necessary was of the order of 20,000 volts. In the following experiments a different method of getting the positive rays was used. Electrons from a Wehnelt cathode C are accelerated in the field CA. They ionize the gas, and the positive particles produced are given a velocity which carries them past the edge of C (2 mm. wide) and through the narrow tube T. These positive particles are then deflected by magnetic and electric fields, and fall on a screen which has a parabolic

slit S. Each constituent of the rays is drawn out into a parabolic curve, and, by increasing the magnetic field, the various parabolas may successively be brought to fall on the slit. When this occurs the charged particles pass through S and give up their charges to the Faraday chamber F. The

Fig. 1.
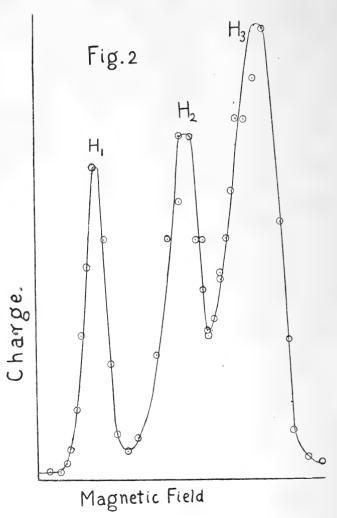
advantages obtained by using a Wehnelt cathode are, that any desired potential may be used, in particular low potentials, and that the pressure of the gas may be made as low as desired and may be varied without changing the potential. The change that occurs in the constituents of the rays as the pressure is decreased is described in this paper.
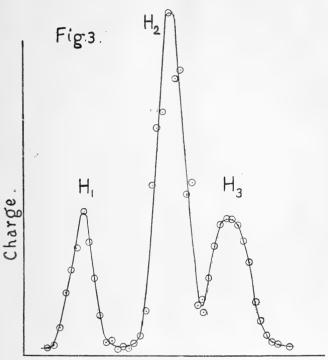
With 800-volt rays and hydrogen at a pressure of about ·01 mm. the curve in fig. 2 was obtained. The abscissæ represent the strength of the deflecting magnetic field, the zero being to the left of the origin, and the ordinates give the charge obtained in the Faraday chamber as the field was increased so as to bring the three lightest constituents of the rays over the parabolic slit. There are present hydrogen atoms, hydrogen molecules, and very much of the constituent with atomic weight 3. The curve obtained with a pressure of ·0017 mm. is given in fig. 3 ; there is a noticeable decrease in the relative amount of both H_1 and H_3. Fig. 4 gives the curve when a charcoal bulb with liquid air was used. Here the pressure was less than ·0005 mm., and H_1 and H_3 have practically disappeared. That this change was due to decreasing pressure, and not to the removal of some constituent of the gas by the charcoal, was shown by the fact that when hydrogen was admitted, while the charcoal and liquid air were on, H_1 and H_3 regained their original relative intensities.

Since in the high vacuum the free path of the molecules is very great, the positives which are still formed by the dense stream of corpuscles coming from the Wehnelt cathode make very few collisions with the hydrogen molecules.

Fig. 2

Hence these positive molecules are analysed in the condition in which they are just after they have been ionized. We must conclude, then, that electrons ionize only by detaching

a single electron from the molecule, and are not able to dissociate the molecule into atoms. When the pressure is greater, some of the positive molecules collide with the molecules of the gas before the cathode, and this collision
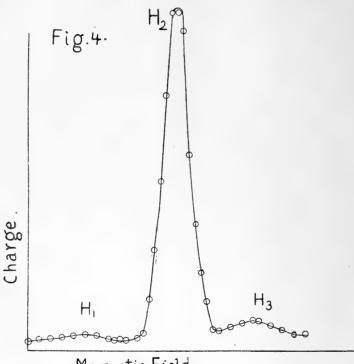
results in a dissociation of the gas into atoms. A positive atom thus formed may attach itself to a neutral molecule and give rise to H_3.

The experiments thus confirm for electrons of this speed the conclusion reached by Millikan from his experiments with oil-drops (Phil. Mag. xxi. p. 753 (1911)) that gaseous ionization produced by β-rays, or by X-rays of all hardnesses, consists in the detachment from a neutral molecule of a single elementary charge. They also verify the theory advanced by J. J. Thomson to account for the results obtained in his experiments on positive rays (Phil. Mag. xxiv. p. 234 (1912)), that the electrons and positive rays produce

different types of ionization. The results show also that H_3 cannot be regarded as a stable gas, but that it is a temporary complex formed only when the hydrogen is in a dissociated state. In his paper in Phil. Mag. xxiv. p. 241 (1912), J. J. Thomson finds that H_3 " occurs under certain conditions

of pressure and current," but later ('Rays of Positive Electricity') regards it as a stable gas which, among other properties, combines with oxygen and mercury when under the influence of the electric discharge. It is possible that the disappearance of H_3 in the latter case is due to a higher vacuum, for I find that the pressure is much reduced when the discharge is passed through mercury-vapour and hydrogen.

Summary.

Electrons of 800 volts speed ionize hydrogen by detaching a single elementary charge from the molecule. They are not able to dissociate the gas.

The positive molecules so formed are able to dissociate the gas. When this occurs the complex H_3 is formed. H_3 cannot be regarded as a stable gas, since it is not present when there is no dissociation of the hydrogen molecules.

Ryerson Physical Laboratory,
University of Chicago,
January 22, 1916.

LIII. *On the Coefficients of Mutual Induction of Eccentric Coils. By* S. BUTTERWORTH, *M.Sc., Lecturer in Physics, School of Technology, Manchester* [*].

1. IN certain types of variable inductances[†] one coil moves so that its plane remains parallel to, and at a constant distance from, the plane of a fixed coil. By this means the mutual induction between the two coils may be made to range from a considerable value to zero and then to change sign during a comparatively small motion of the coil. This use of eccentric coils lends a certain interest to the problem of determining the mutual induction between two non-coaxial circular filaments.

2. The principle to be made use of is to treat the mutual induction between the two circles as a potential function of the position of the centre of the moving circle. The proof of this is as follows :—

Replace the moving circle by its equivalent magnetic shell and consider the variation in potential energy of this shell as it moves in the magnetic field due to the current in the fixed circle. It is clear that the variation in potential energy of the individual particles of the shell follows the law of potential, so that, since for motions of translation the displacement of every particle is the same, the potential energy of the whole shell also varies in accordance with the law of potential. Identifying the potential energy of the shell with the mutual induction between the two circles, the proposition is proved.

For parallel circles the mutual induction (regarded as a potential function) has a symmetrical distribution about the axis of the fixed circle, so that if the mutual induction is known in the coaxial position the mutual induction in any other position can be derived by the usual methods for determining potential.

[*] Communicated by the Author.
[†] Campbell, Phil. Mag. xv. p. 155 (1908).

3. *Equal Circles.*

Take the radius of either circle as the unit of length and let x be the distance of their planes. Then when x is large and the circles are coaxial, the mutual inductance is [*]

$$\mathrm{M}_0 = \frac{2\pi^2}{x^3}\left(1 - \frac{3}{4x^2} + \frac{25}{24x^4} - \frac{245}{128x^6} + \cdots\right), \quad . \quad (1)$$

the multiplying factor to obtain the nth term from the preceding term being

$$-\frac{1}{x^2}\left(\frac{2n-1}{n}\right)^2 \frac{n-1}{n+1}.$$

Hence, using spherical coordinates with the centre of the fixed circle as origin and its axis as the axis of coordinates, when the centre of the moving circle is at r, θ the mutual inductance is

$$\mathrm{M} = \frac{2\pi^2}{r^3}\left(\mathrm{P}_2 - \frac{3}{4}\frac{\mathrm{P}_4}{r^2} + \frac{25}{24}\frac{\mathrm{P}_6}{r^4} - \frac{245}{128}\frac{\mathrm{P}_8}{r^6} + \cdots\right), \quad (2)$$

in which $\mathrm{P}_n \equiv \mathrm{P}_n(\cos\theta)$ is the zonal harmonic of order n.

When the circles are coplanar, $\theta = \frac{\pi}{2}$, and (2) then becomes

$$\mathrm{M}_1 = -\frac{\pi^2}{r^3}\left(1 + \frac{9}{16r^2} + \frac{125}{192r^4} + \frac{8575}{8192r^6} + \cdots\right), \quad (3)$$

the multiplying factor to obtain the nth term being

$$\frac{1}{2r^2}\left(\frac{2n-1}{n}\right)^3 \frac{n-1}{n+1}.$$

Formulæ (1), (2), and (3) converge if $r > 2$, but the convergence is rather slow if r is less than 3.

When x is small and the circles are coaxial the mutual induction is [†]

$$\mathrm{M}_0 = 4\pi\left\{\lambda_0 - 2 + \frac{3}{16}x^2\left(\lambda_0 - \frac{1}{3}\right) - \frac{15x^4}{1024}\left(\lambda_0 - \frac{31}{30}\right)\right.$$
$$\left. + \frac{35}{(128)^2}x^6\left(\lambda_0 - \frac{247}{210}\right) - \cdots\right\}, \quad (4)$$

in which $\lambda_0 = \log_e \frac{8}{x}.$

To obtain the mutual induction for non-coaxial circles

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[*] Havelock, Phil. Mag. xv. p. 332 (1908).

[†] Coffin, Bull. Bureau of Standards, ii. p. 113 (1906); Havelock, *loc. cit.*

from this formula we must replace the terms x^n by $r^n \mathrm{P}_n$ and the terms $x^n \log_e x$ by

$$\frac{\partial}{\partial n}(r^n \mathrm{P}_n) \equiv r^n \left(\mathrm{P}_n \log_e r + \frac{\partial \mathrm{P}_n}{\partial n} \right),$$

for these clearly satisfy Laplace's Equation, and since

$$\frac{\partial \mathrm{P}_n}{\partial n} = 0, \quad \mathrm{P}_n = 1 \quad \text{when } \theta = 0,$$

they reduce to x^n and $x^n \log_e x$ respectively when $\theta = 0$.

In applying this transformation the following explicit values of $\dfrac{\partial \mathrm{P}_n}{\partial n}$ are required:

$$\frac{\partial \mathrm{P}_n}{\partial n} = \mathrm{P}_n \log_e \tfrac{1}{2}(1+\mu) + \psi_n, \quad . \quad . \quad . \quad (5)$$

in which $\mu = \cos \theta,$

$$\psi_n = 2 \left\{ \frac{2n-1}{1 \cdot 2n} (\mathrm{P}_n - \mathrm{P}_{n-1}) - \frac{2n-3}{2(2n-1)}(\mathrm{P}_n - \mathrm{P}_{n-2}) \right.$$
$$\left. + \ldots + (-)^{n+1} \frac{1}{n(n+1)}(\mathrm{P}_n - \mathrm{P}_0) \right\}, \quad . \quad (6)$$

and in particular

$$\left.\begin{aligned}
\psi_0 &= \quad 0, \\
\psi_2 &= -\frac{1}{4}(1-\mu)(1+7\mu), \\
\psi_4 &= \quad \frac{1}{96}(1-\mu)(21+241\mu-113\mu^2-533\mu^3), \\
\psi_6 &= -\frac{1}{960}(1-\mu)(185-2957\mu+3728\mu^2+18008\mu^3 \\
&\qquad\qquad\qquad -3247\mu^4-18107\mu^5).
\end{aligned}\right\} \quad . \quad (7)$$

On making the necessary substitutions in (4) the required mutual induction is given by

$$\frac{\mathrm{M}}{4\pi} = \lambda - 2 + \frac{3}{16} r^2 \left\{ \mathrm{P}_2 \left(\lambda - \frac{1}{3} \right) - \psi_2 \right\}$$
$$- \frac{15}{1024} r^4 \left\{ \mathrm{P}_4 \left(\lambda - \frac{31}{30} \right) - \psi_4 \right\}$$
$$+ \frac{35}{(128)^2} r^6 \left\{ \mathrm{P}_6 \left(\lambda - \frac{247}{210} \right) - \psi_6 \right\}$$
$$- \ldots \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8),$$

in which $\lambda = \log_e \dfrac{16}{r(1+\mu)}.$

For purposes of computation it is convenient to write (8)

$$\frac{M}{4\pi} = \alpha_0 + \alpha_1 r^2 + \alpha_2 r^4 + \alpha_3 r^6 + \ldots$$
$$- \log_e r(1 + \beta_1 r^2 + \beta_2 r^4 + \beta_3 r^6 + \ldots) \quad . \quad . \quad (9)$$

and to tabulate $\alpha_0, \alpha_1 \ldots, \beta_1 \ldots$ as functions of μ. This is done in Table I.

When $\mu = 0$ the circles are coplanar and (8) reduces to

$$\frac{M_1}{4\pi} = \lambda_1 - 2 - \frac{3}{32} r^2 \left(\lambda_1 - \frac{5}{6}\right) - \frac{45}{8192} r^4 \left(\lambda_1 - \frac{97}{60}\right)$$
$$- \frac{175}{(512)^2} r^6 \left(\lambda_1 - \frac{251}{140}\right) - \ldots \quad . \quad . \quad (10)$$

in which $\qquad \lambda_1 = \log_e \dfrac{16}{r}.$
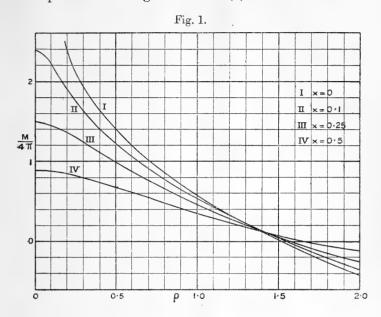
Formulæ (4), (8), and (10) converge fairly rapidly so long as r is less than unity. They will give a rough approximation up to $r = 1.6$ but fail for larger values.

TABLE I.

Values of coefficients in formula (9).

μ.	α_0.	α_1.	α_2.	α_3.	β_1.	β_2.	β_3.
0·0	0·7726	−0·1817	−0·00487	−0·00066	−0·0938	−0·00549	−0·00067
0·1	0·6773	−0·1414	−0·00217	−0·00009	−0·0909	−0·00495	−0·00053
0·2	0·5903	−0·0962	+0·00208	+0·00071	−0·0825	−0·00340	−0·00017
0·3	0·5102	−0·0473	+0·00577	+0·00107	−0·0684	−0·00107	+0·00028
0·4	0·4361	+0·0044	+0·00829	+0·00098	−0·0488	+0·00166	+0·00063
0·5	0·3671	+0·0578	+0·00921	+0·00045	−0·0234	+0·00424	+0·00069
0·6	0·3026	+0·1123	+0·00818	−0·00021	+0·0075	+0·00597	+0·00037
0·7	0·2420	+0·1671	+0·00507	−0·00090	+0·0441	+0·00604	−0·00027
0·8	0·1848	+0·2216	−0·00006	−0·00098	+0·0862	+0·00341	−0·00084
0·9	0·1308	+0·2752	−0·00701	−0·00019	+0·1341	−0·00305	−0·00052
1·0	0·0795	+0·5274	−0·01531	+0·0017	+0·1875	−0·01462	+0·00214

4. In order to test whether the formulæ are adequate to represent the mutual induction for the range which is most useful in practice, *i. e.* from the coaxial position to the position where the mutual induction is zero, Table II. has been prepared. In this table, x is the distance of the planes of the circles and ρ the distance of their axes, the radii of the two circles being unity. The results are plotted in

fig. 1. It is seen that the induction changes sign when ρ is less than 1·7 in all the cases taken. This practically corresponds to the range of formula (9).

Fig. 1.

TABLE II.

Mutual induction between equal parallel circles.
Radii of circles = unit of length.
x = distance of planes; ρ = distance of axes.

$x=0.$				$x=0.1.$		$x=0.25.$		$x=0.5.$	
$\rho.$	M/4$\pi.$	$\mu.$	$\rho.$	M/4$\pi.$	$\rho.$	M/4$\pi.$	$\rho.$	M/4$\pi.$	
0	infinity	1·0	0	2·39	0	1·50	0	0·88	
0·2	2·37	0·9	0·05	2·34	0·121	1·45	0·24	0 83	
0·4	1·65	0·8	0·075	2·27	0·188	1·38	0·37	0·76	
0·6	1·20	0·7	0·102	2·19	0·256	1·30	0·51	0·67	
0·8	0·86	0·6	0·133	2·10	0·334	1·20	0·67	0·57	
1·0	0·58	0·5	0·173	1·98	0·433	1·07	0·87	0·43	
1·2	0·33	0·4	0·229	1·82	0·573	0·90	1·15	0·26	
1·4	0·12	0·3	0·318	1·60	0·796	0·65	1·59	0·03	
1·6	−0·17	0·25	...	...	...	...	1·94	−0·10	
1·8	...	0·2	0·49	1·24	1·225	0·26	...	...	
2·0	−0·43	0·125	...	...	1·98	−0·24	...	...	
		0·1	1·00	0·53	...	...	...	...	
		0·05	2·00	−0·36	...	...	...	...	

5. *Unequal circles.*

Let the radii of the circles be a and A and let x be the distance of their planes. Then if x is large and the circles are coaxial, the mutual induction is *

$$M_0 = \frac{2\pi^2 a^2 A^2}{x^3}\left(1 - \frac{3}{2}\frac{A^2}{x^2}K_1 + \frac{3 \cdot 5}{2 \cdot 4}\frac{A^4}{x^4}K_2 - \frac{3 \cdot 5 \cdot 7}{2 \cdot 4 \cdot 6}\frac{A^6}{x^6}K_3 + \dots\right), \quad (11)$$

in which

$$\left.\begin{array}{l}
K_1 = 1 + \dfrac{a^2}{A^2}, \\[2mm]
K_2 = 1 + 3\dfrac{a^2}{A^2} + \dfrac{a^4}{A^4}, \\[2mm]
K_3 = 1 + 6\dfrac{a^2}{A^2} + 6\dfrac{a^4}{A^4} + \dfrac{a^6}{A^6}, \\[2mm]
\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\[2mm]
K_n = F\left(-n-1, \quad -n, \quad 2, \quad \dfrac{a^2}{A^2}\right),
\end{array}\right\}$$

where $F(\alpha, \beta, \gamma, z)$ denotes the hypergeometric series

$$1 + \frac{\alpha\beta}{1 \cdot \gamma}z + \frac{\alpha(\alpha+1)\beta(\beta+1)}{1 \cdot 2\,\gamma(\gamma+1)}z^2 + \dots.$$

Hence for non-coaxial circles the mutual induction is

$$M = \frac{2\pi^2 a^2 A^2}{r^3}\left(P_2 - \frac{3}{2}\frac{A^2}{r^2}K_1 P_4 + \frac{3 \cdot 5}{2 \cdot 4}\frac{A^4}{r^4}K_2 P_6 - \frac{3 \cdot 5 \cdot 7}{2 \cdot 4 \cdot 6}\frac{A^6}{r^6}K_3 P_8 + \dots\right), \quad (12)$$

reducing for coplanar circles to

$$M_1 = -\frac{\pi^2 a^2 A^2}{r^3}\left(1 + \frac{3^2}{2 \cdot 4}\frac{A^2}{r^2}K_1 + \frac{3^2 \cdot 5^2}{2 \cdot 4^2 \cdot 6}\frac{A^4}{r^4}K_2 \right.$$
$$\left. + \frac{3^2 \cdot 5^2 \cdot 7^2}{2 \cdot 4^2 \cdot 6^2 \cdot 8}\frac{A^6}{r^6}K_3 + \dots\right). \quad (13)$$

Formulæ (11), (12), and (13) converge if $r > A + a$, *i.e.* in formula (13) if one circle is entirely outside the other.

When x is small it is convenient to choose the difference in radii of the two circles as the unit of length. Then,

* Havelock, *loc. cit.*

when the circles are coaxial *,

$$M_0 = 4\pi\sqrt{Aa}\left\{ \lambda_0 - 2 + \frac{3}{16}\frac{(1+x^2)}{Aa}\left(\lambda_0 - \frac{1}{3}\right)\right.$$
$$\left. - \frac{15}{1024}\frac{(1+x^2)^2}{A^2a^2}\left(\lambda_0 - \frac{31}{30}\right) + \ldots\right\}, \quad (14)$$

in which $\qquad \lambda = \log_e \dfrac{8\sqrt{Aa}}{\sqrt{1+x^2}}.$

The transformation of (14) to the formula for the non-coaxial case requires the determination of a solution of Laplace's equation, which will reduce to

$$(1+x^2)^m \log_e \sqrt{1+x^2}$$

at all points on the axis of x. This solution will now be found.

6. In cylindrical coordinates (x, ρ, ϕ) and with $\dfrac{\partial^2 V}{\partial \phi^2} = 0$, Laplace's equation is

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial V}{\partial \rho} = 0. \quad . \quad . \quad . \quad . \quad (15)$$

Transforming to spheroidal coordinates by putting

$$x = \mu\nu, \quad \rho = (1-\mu^2)^{\frac{1}{2}}(1+\nu^2)^{\frac{1}{2}}, \quad . \quad . \quad (15\,a)$$

(15) becomes

$$\frac{\partial}{\partial\mu}\left\{(1-\mu^2)\frac{\partial V}{\partial\mu}\right\} + \frac{\partial}{\partial\nu}\left\{(1+\nu^2)\frac{\partial V}{\partial\nu}\right\} = 0, \quad . \quad (16)$$

a possible solution of which is

$$V = \frac{\partial}{\partial n}\{P_n(\mu)P_n(i\nu)\} - P_n(\mu)Q_n(i\nu)$$
$$- \Sigma A_s P_s(\mu)P_s(i\nu), \quad . \quad (17)$$

in which $i = \sqrt{-1}.$

When $\mu = 1$, that is, when $\rho = 0$, $\nu = x$, (17) reduces to

$$V = \frac{\partial P_n(i\nu)}{\partial n} - Q_n(i\nu) - \Sigma A_s P_s(i\nu). \quad . \quad . \quad (18)$$

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* Havelock, *loc. cit.*; Rosa, Bull. Bureau of Standards, viii. p. 15 (1912).

Since

$$Q_n(z) = \tfrac{1}{2} P_n \log \frac{1+z}{1-z} - \frac{2n-1}{1 \cdot n} P_{n-1} + \frac{2n-5}{3(n-1)} P_{n-3}$$

$$- \frac{2n-9}{5(n-2)} P_{n-5} + \ldots$$

and

$$\frac{\partial P_n(z)}{\partial z} = P_n \log \tfrac{1}{2}(1+z)$$

$$+ 2 \left\{ \frac{2n-1}{1 \cdot 2n} (P_n - P_{n-1}) - \frac{2n-3}{2(2n-1)} (P_n - P_{n-2}) \right.$$

$$\left. + \frac{2n-5}{3(2n-2)} (P_n - P_{n-3}) - \ldots \right\},$$

the logarithmic term in (18) is

$$P_n(i\nu) \log \tfrac{1}{2} \sqrt{1+\nu^2}.$$

Also, if s takes the values n, $n-2$, $n-4$, ... and

$$\left. \begin{aligned} A_n &= \log \tfrac{1}{2} + 2 \left\{ \frac{2n-1}{1 \cdot 2n} - \frac{2n-3}{2(2n-1)} + \frac{2n-5}{3(2n-2)} - \ldots \right\} \\ A_{n-2} &= \frac{2n-3}{2n-1}, \quad A_{n-4} = \frac{2n-7}{2n-3}, \quad \ldots \ldots \end{aligned} \right\} \quad (19)$$

the value of V along the axis of symmetry becomes

$$P_n(ix) \log \sqrt{1+x^2}.$$

Therefore to obtain the solution sought it only remains to expand $(1+x^2)^m$ in a series involving $P_n(ix)$ and to apply the results (17) and (19) to each term of this series.

The series in question is

$$(1+x^2)^m = (-)^m 2^m \underline{|m} \frac{1 \cdot 3 \ldots 2m-1}{1 \cdot 3 \ldots 4m+1} \left\{ (4m+1) P_{2m}(ix) \right.$$

$$- (4m-3) \frac{m}{\underline{|1}} \cdot \frac{4m+1}{2m-1} P_{2m-2}(ix)$$

$$\left. + (4m-7) \frac{m(m-1)}{\underline{|2}} \cdot \frac{(4m+1)(4m-1)}{(2m-1)(2m-3)} P_{2m-4}(ix) - \ldots \right\}, \quad (20)$$

from which

$$\left. \begin{aligned} 1+x^2 &= -\frac{2}{3} P_2(ix) + \frac{2}{3} P_0(ix), \\ (1+x^2)^2 &= \frac{8}{35} P_4(ix) - \frac{16}{21} P_2(ix) + \frac{8}{15} P_0(ix). \end{aligned} \right\} \quad (21)$$

7. On applying the results of Section 6 to (14) and inserting the values of $P_n(\mu)$, $P_n(i\nu)$, the mutual induction between non-coaxial circles is found to be

$$M = 4\pi\sqrt{Aa}\left[\lambda - 2 + \frac{3}{16}\frac{1}{Aa}\left\{\left(\lambda - \frac{1}{3}\right)\phi_2 - \chi_2\right\}\right.$$
$$\left. - \frac{15}{1024}\frac{1}{A^2a^2}\left\{\left(\lambda - \frac{31}{30}\right)\phi_4 - \chi_4\right\} + \ldots\right], \qquad (22)$$

in which

$$\lambda = \log_e\frac{16\sqrt{Aa}}{(1+\mu)\sqrt{1+\nu^2}},$$

$$\phi_2 = \frac{2}{3} - \frac{2}{3}P_2(\mu)P_2(i\nu)$$

$$= \frac{1}{2}\{(1+\mu^2) - \nu^2(1-3\mu^2)\},$$

$$\phi_4 = \frac{8}{15} - \frac{16}{21}P_2(\mu)P_2(i\nu) + \frac{8}{35}P_4(\mu)P_4(i\nu)$$

$$= \frac{1}{8}\{(3+2\mu^2+3\mu^4) - 2\nu^2(1+6\mu^2-15\mu^4)$$
$$+ \nu^4(3-30\mu^2+35\mu^4)\},$$

$$\chi_2 = \frac{1}{4}(1-\mu)\{(1-\mu) - \nu^2(1+7\mu)\},$$

$$\chi_4 = \frac{1}{96}(1-\mu)\{3(1-\mu)(7+2\mu+7\mu^2)$$
$$- 6\nu^2(5-\mu-\mu^2+59\mu^3)$$
$$+ \nu^4(21+241\mu-113\mu^2-533\mu^3)\},$$

and from (15 a)

$$\mu^2, \; -\nu^2 \text{ are the roots of}$$
$$t^2 - t(1-\rho^2-x^2) - x^2 = 0. \quad . \quad . \quad . \quad . \quad (23)$$

In (22) the difference in the radii of the two circles is unity. If $A\sim a = c$, then replace in (22) $1/Aa$ by c^2/Aa, multiply by c, and make μ^2, $-\nu^2$ the roots of

$$c^2t^2 - t(c^2-\rho^2-x^2) - x^2 = 0. \quad . \quad . \quad (23\,a)$$

To test the formula, let c approach zero. The limiting value of μ is $x/\sqrt{x^2+\rho^2} \equiv x/r$, and that of $c\nu$ is r. Using these in (22), we obtain formula (7).

8. When $x=0$ the circles are coplanar.

If $r>c$, $\mu=0$, $\nu^2=\dfrac{r^2}{c^2}-1$ and the mutual induction is

$$M_1=4\pi\sqrt{Aa}\Big[\lambda_1-2-\frac{3}{32}\frac{r^2}{Aa}\Big(\lambda_1-\frac{5}{6}\Big)\Big(1-\frac{2c^2}{r^2}\Big)$$
$$-\frac{45}{8192}\frac{r^4}{A^2a^2}\Big\{\lambda_1\Big(1-\frac{8}{3}\frac{c^2}{r^2}+\frac{8}{3}\frac{c^4}{r^4}\Big)$$
$$-\Big(\frac{97}{60}-\frac{214}{45}\frac{c^2}{r^2}+\frac{214}{45}\frac{c^4}{r^4}\Big)\Big\}-\dots\Big],$$

$$. \quad . \quad (24)$$

in which
$$\lambda_1=\log_e\frac{16\sqrt{Aa}}{r}.$$

This formula holds good when the two circles intersect.

If $r<c$, $\nu=0$, $\mu^2=1-\dfrac{r^2}{c^2}$, and the mutual induction is

$$M_1'=4\pi\sqrt{Aa}\Big[\lambda_1'-2+\frac{3}{32}\frac{c^2}{Aa}\Big\{\Big(\lambda_1'-\frac{1}{3}\Big)(1+\mu^2)-\frac{1}{2}(1-\mu)^2\Big\}$$
$$-\frac{15}{8192}\frac{c^4}{A^2a^2}\Big\{\Big(\lambda_1'-\frac{31}{30}\Big)(3+2\mu^2+3\mu^4)$$
$$-\frac{1}{4}(1-\mu)^2(7+2\mu+7\mu^2)\Big\}+\dots\Big],$$

$$. \quad . \quad . \quad (25)$$

in which
$$\lambda_1'=\log_e\frac{16\sqrt{Aa}}{c(1+\mu)}.$$

This formula holds when one circle is entirely inside the other.

If $r=c$, the two circles touch internally and the mutual induction is

$$M_1''=4\pi\sqrt{Aa}\Big\{\lambda_1''-2+\frac{3}{32}\frac{c^2}{Aa}\Big(\lambda_1''-\frac{5}{6}\Big)-\frac{45}{8192}\frac{c^4}{A^2a^2}\Big(\lambda_1''-\frac{97}{60}\Big)$$
$$+\dots\Big\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$
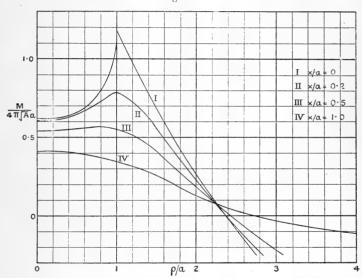
in which
$$\lambda_1''=\log_e\frac{16\sqrt{Aa}}{c}.$$

It is interesting to notice the similarity between formulæ (26) and (10).

9. The formulæ for unequal circles close together do not readily admit of simplification even with the aid of tables. The following calculations (Table III.) have been made to test the range of the formulæ. The ratio $A/a = 2$ has been chosen so as to compare the results with the experimental curves of Campbell (*loc. cit.*). Otherwise it is not a very favourable ratio for the formulæ. The curves obtained (fig. 2) show very good agreement with the experimental

Fig. 2.

curves and give approximately the same zero points. The separate terms are tabulated so as to indicate their relative importance. The labour involved in obtaining the third term is altogether out of proportion with the importance of that term, especially as in the cases where it is large the fourth and succeeding terms are likely to have an appreciable effect. It will be found that for most purposes the first two terms only in the formulæ need be used. It will also be noticed that in the most important range of the curves (viz., from $\rho/a = 1$ to $M = 0$) the curvature is slight, so that after calculating a few points within this range from the theoretical formulæ, an empirical formula of the type

$$M = \alpha_0 + \alpha_1 \frac{\rho}{a} + \alpha_2 \frac{\rho^2}{a^2} + \ldots$$

should be sufficient to determine intermediate values.

TABLE III.

Mutual induction between unequal circles.

$$A = 2a.$$

	$x/a=0.$					$x/a=0.2.$			
$\frac{\rho}{a}$.	1st Term.	2nd Term.	3rd Term.	$\frac{M}{4\pi\sqrt{Aa}}$.	$\frac{\rho}{a}$.	1st Term.	2nd Term.	3rd Term.	$\frac{M}{4\pi\sqrt{Aa}}$.
0·00	0·426	0·196	−0·005	0·617	0·00	0·406	0·202	−0·005	0·603
0·60	0·521	0 167	−0·003	0·685	0·45	0·453	0·187	−0·005	0·635,
0·80	0·649	0·144	−0·003	0·790	0·62	0·501	0·174	−0·004	0·671
0·92	0·783	0·125	−0·002	0·906	0·74	0·548	0·160	−0·003	0·705
0·98	0·937	0·112	−0·002	1·047	0·84	0·597	0·147	−0·003	0·741
1·00	1·119	0·107	−0·002	1·224	0·93	0·640	0·133	−0·002	0·771
1·41	0·773	0·000	−0·003	0·770	1·02	0·671	0·118	−0·002	0·787
1·73	0·570	−0·085	−0·006	0·479	1·15	0·673	0 074	−0·001	0·746
2·00	0·426	−0·149	−0·011	0·266	1·39	0·591	0·047	−0·000	0·638
2·24	0·314	−0·208	−0·016	0·090	2·22	0·220	−0·129	+0·000	0·091
2·45	0·223	−0·260	−0·022	−0·059	2·69	0·052	−0·225	+0·001	−0·172

	$x/a=0.5.$					$x/a=1.0.$			
0·00	0·314	0·232	−0·007	0·539	0·00	0·089	0·330	−0·015	0·404
0·50	0·342	0·216	−0·007	0·551	0·65	0·075	0·313	−0·008	0·380
0·71	0·366	0·202	−0 005	0·563	0·96	0·061	0·297	−0·003	0·355
0·88	0·382	0·185	−0·003	0·564	1·24	0·032	0·280	−0·001	0·311
1·04	0·385	0·165	−0·001	0·549	1·53	−0·002	0·250	+0·010	0·258
1·22	0·367	0·142	+0·001	0·510	1·94	−0·091	0·213	+0·028	0·150
1·47	0·313	0·107	+0·004	0·424	2·47	−0·207	0·184	+0·068	0 045
1·86	0·192	0·045	+0·012	0·249	3·32	−0·392	0·133	+0·200	−0·059
2·64	−0·053	−0·070	+0·042	−0·081					

LIV. *Magnetic Rotary Dispersion in Relation to the Electron Theory.*—Part II. *The Number of Electrons and Additive Relations.* By S. S. RICHARDSON, B.Sc., A.R.C.Sc., Lecturer in Physics, Central Technical School, Liverpool* [*].

ONE of the problems arising from the theory of electrons is the determination, from optical data, of the number of resonators present in the molecule of a substance. The subject has been examined by Reiff [†], Lorentz [‡], Drude [§], and Erfle [∥] in connexion with the dispersion constants, and by Kœnigsberger and Kilchling [¶] with respect to the

constant of absorption. The present paper deals with the application of magnetic rotary dispersion to the elucidation of the same problem.

If N denotes the number of resonators present in the unit of volume, p the number per molecule, m the mass and e the charge of each; d the density and M the molecular weight of the substance; and h the absolute mass of the hydrogen atom: then

$$N_1 e_1 = p_1 \cdot \frac{d}{M} \cdot \frac{e_1}{h}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

The ratio of e_1 to h, if we confine our attention to electrons, is equivalent to the electrolytic constant—96530 coulombs or $9653 \times 3 \times 10^{10}$ electrostatic units per gram.

When $N_1 e_1$ can be obtained from optical data, (1) gives at once the value of p_1.

(A) *Number of Electrons deduced from Natural Dispersion.*—In the case of ordinary dispersion we may write

$$n^2 - 1 = \Sigma \frac{a_1 \lambda^2}{\lambda^2 - \lambda_1{}^2}.$$

According to Drude's theory, λ_1 is the wave-length corresponding to the free-period of the vibrator and

$$a_1 = \frac{N_1 e_1{}^2 \lambda_1{}^2}{\pi m_1 C^2}.$$

This expression for a_1 holds good also in the theory of Lorentz and Planck, but λ_1 is less than the wave-length λ_f corresponding to the free period, the two being connected by the equation

$$\lambda_1{}^2 = \frac{\lambda_f{}^2}{1-g}; \quad \text{where } g = \frac{1}{3} \frac{N_1 e_1{}^2 \lambda_f{}^2}{\pi m_1 C^2}.$$

In either case, therefore, if λ_1 is the wave-length of the dispersional period, determined from the course of the dispersion-curve,

$$N_1 e_1 = \frac{\pi a_1 C^2}{\lambda_1{}^2} \bigg/ \frac{e_1}{m_1}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

When the constants $a_1, a_2 \ldots, \lambda_1, \lambda_2 \ldots$, have been completely determined, equations (1) and (2) can be applied to evaluate p_1, p_2, &c. This, however, is not in general practicable, as the value of the dispersional period is as a rule only an effective mean. This is particularly the case when λ_1, λ_2, &c., lie in the Schumann region.

In the visible and ultraviolet the effect of infra-red bands is very small, and can be represented by a term $-c\lambda^2$.

Thus

$$n^2 - 1 = \Sigma \frac{a_1 \lambda^2}{\lambda^2 - \lambda_1^2} - c\lambda^2,$$

where the terms under the summation sign refer to ultraviolet resonators only (electrons). Drude (*loc. cit.*) shows that if we confine our attention to this case, we may determine a lower limit to the number of electrons affecting the refractive index. If x_1, x_2 denote the reciprocals of the squares of two wave-lengths in the visible or ultraviolet and r_1, r_2 the values of

$$n^2 - 1 + c\lambda^2$$

for these wave-lengths, and if

$$d_{12} = \frac{r_1 - r_2}{x_1 - x_2},$$

then the lower limit referred to is given by the inequality

$$\frac{e}{m}(p_1 + p_2 + \ldots) \geqq 9{\cdot}78 \times 10^6 \frac{M}{d} \cdot \frac{r_1 r_2}{d_{12}}. \quad . \quad . \quad (3)$$

Drude has applied equation (3) to the data for a large number of organic and several inorganic compounds, and arrives at the conclusion that "the number of electrons in the molecule which influence the refractive index is equal to the sum of the valencies of the several atoms in the molecule."

Similar calculations have been made by Erfle for a number of aromatic and other unsaturated compounds.

The following table will suffice to indicate the general character of the numerical results.

TABLE I.

(Drude.)	$v.$	$p.$	(Erfle.)	$v.$	$p.$
Fluorite	4 (16)	9·5	Amylene	30	15·3
Quartz	8 (16)	8·2	Propargyl alcohol	18 (22)	9·9
Carbon bisulphide	8 (16)	7·3	Tribrom-ethylene	12 (30)	15·7
Water	4 (8)	3·9	Naphthalene	48	13·9
Sylvine	2 (8)	7·6	Triethylamine	42 (44)	23·3
Rock-salt	2 (8)	5·6	Silicon bromide	8 (32)	21·6
Methyl alcohol	10 (14)	8·4	Hexapropyl disilicate	136 (164)	90·5
Ethyl alcohol	16 (20)	12·5	Tetramethyl silicate	40 (56)	29·9
Benzene	30	12·0	Hydroxylamine	8 (14)	5·5
Toluene	36	14·8	Diamond	4	2·7
Xylene	42	17·6	Hydrogen	2	1·9
Cane-sugar	92 (136)	149	Nitrogen	6 (10)	4·5

Here v is the total number of valencies in the molecule and p is the number of electrons calculated with $e/m = 4.5 \times 10^{17}$ e.s.u., which is somewhat smaller than the normal value.

In the above no attempt is made to distinguish between the resonators which influence the refraction but have no measurable effect on the dispersion and those to which the dispersion is due. This of course can only be done when from an extended series of measurements of n the constants a have been calculated. There are a few substances for which these constants have been determined. The results for these, recalculated for the normal value of $e/m(5.325 \times 10^{17})$, are given below.

TABLE II.

Substance.	v.	p_1.	Substance.	v.	p_1.
Quartz	8 (16)	3·94	Water	4 (8)	·88
Fluorite	4 (16)	3·49	Carbon bisulphide	8 (16)	1·93
Sylvine	2 (8)	1·92	Benzene	30	3·35
Rock-salt	2 (8)	3·54	Naphthalene bromide.	48 (54)	3·06
Calc spar (ord.)	12 (24)	4·42	Methyl iodide	8 (14)	2·90

As λ_1 in the formulæ is a mean value, the above numbers give the upper limit to the number of electrons of longest ultraviolet free period, except in so far as the unknown value of e/m may affect the result. The values of pe/m used for the first seven substances are those calculated by Drude, and for the last three those of Erfle. The refraction measurements of Erfle were confined to the visible spectrum, but carried to a high degree of accuracy, and the constants obtained do not differ notably from those given in Part I. of this paper.

Drude concludes that "the number of electrons in the molecule which influence the dispersion is equal to or less than the sum of the valencies of the atoms."

(B) *Number of Electrons deduced from Magnetic Rotation.*— It has been shown in Part I. that the only electrons influencing the magnetic rotation are those whose periods are sufficiently long to affect the dispersion, and the magnetic property therefore provides an alternative method of estimating the number of electrons of this type. Before proceeding to deduce the formula we must give certain secondary effects some further consideration.

Voigt's theory of magnetic rotation and birefringence, which attributes the two phenomena to essentially the same cause, fails to account quantitatively for the latter property in liquids, the observed value being some 10^3 times as great as that calculated. Cotton and Mouton & Langevin [*] have shown that the property of magnetic birefringence is satisfactorily explained by a molecular orientation set up by the magnetic field,—a theory which also accounts for the rapid decrease in the effect with rise of temperature. Now such orientation may bring into play intermolecular forces, either electrical or magnetic, and influence the periods of vibration of the resonators. As a first approximation the variation in the magnetic rotation so produced may be represented by a virtual change in the dispersion constants, which therefore become $(a + a\xi H^2)$. The experiments of Cotton and Mouton have shown that among organic liquids the magnetic double refraction is exhibited most strongly by the unsaturated and aromatic compounds, saturated and aliphatic substances showing scarcely any trace of the effect. It is therefore reasonable to expect that the value of ξ will be negligible for liquids of the latter class. Voigt's theory suffices to explain the birefringence in metallic vapours, and ξ may be taken as zero for substances in the gaseous state. We may also regard it as inoperative in solids, for the applied field is always very small in comparison with the intense intermolecular fields brought into play during crystallization. From the change in diamagnetic susceptibility during the solidification, Oxley finds the latter equivalent to magnetic fields of the order 10^7 gauss. It may be added that the hypothesis of intermolecular fields is not essential to the theory. The *effective* free periods of an assemblage of æolotropic molecules when these are partially orientated by the field may be expected to differ from the effective periods of the same molecules when their indiscriminate motions render the medium as a whole isotropic. Thus, apart from the change $eH/2mC$ directly imposed by the field, the change in the effective period will influence the rotation, which will therefore differ from that calculated in terms of the dispersion constants of the *isotropic* medium, and this influence we may also attempt for the present to express by ξ. As we have seen above, it is probably only in unsaturated compounds that it may be great enough to be measurable, and in general therefore it can be omitted.

In the formulæ e/m has been taken to have different values for electrons of different frequencies. The velocity of the vibrating electron is so small in comparison with that

[*] *Le Radium,* Sept. 1910.

of radiation, that of course no appreciable variation of electro-magnetic mass is to be expected from this cause; but the mutual action of neighbouring electrons may increase their effective mass, and it is preferable, for the sake of generality, to retain separate values for e/m. If we write $\eta e/m$ for the effective ratio, where e/m is the normal value deduced from the Zeeman effect in gases ($5\cdot325 \times 10^{17}$ e.s.u.), and retain only this normal value within the constants $a_1, a_2 \ldots, k_1, k_2 \ldots$, the equations for refraction and magnetic rotation may be written

$$n^2 - 1 = a_0 + \eta_1 a_1 \frac{\lambda^2}{\lambda^2 - \lambda_1^2} + \eta_2 a_2 \frac{\lambda^2}{\lambda^2 - \lambda_2^2}. \qquad (6)$$

$$\phi = \frac{1}{2C^2} \left\{ \eta_1^2 b_1 (1 + \zeta_1) \frac{e}{m} \left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2} \right)^2 + \eta_2^2 b_2 (1 + \zeta_2) \frac{e}{m} \left(\frac{\lambda^2}{\lambda^2 - \lambda_2^2} \right)^2 \right\}. \qquad (7)$$

The factor ζ, as mentioned in Part I., represents the effect of the impressed field on the intramolecular fields. It may also be taken to include the influence of the impressed field on electronic coupling, such as would give rise to abnormal Zeeman resolution.

It has been shown that the mean value of the dispersional period deduced from magnetic rotation may be smaller than that obtained from natural dispersion. When $\zeta = 0$ we may conclude that this result indicates that η is smaller for longer periods than for short ones; for if $\lambda_1, \lambda_2 \ldots$ are in order of diminishing magnitude, η_2^2 will have greater weight in comparison with η_1^2 than η_2 has in comparison with η_1. The effective value of e/m is always less than the normal value, and η is therefore always less than unity.

In proceeding to obtain an expression for p we may omit ζ, bearing in mind that the result will need modification if this factor is operative.

We have

$$\eta_1 a_1 = N_1 \frac{e^2}{\pi C^2 m} \lambda_1^2 \eta_1$$

and

$$\frac{\eta_1^2 b_1 e}{2 C^2 m} = N_1 \frac{\pi}{2e} \left(\frac{e^2}{\pi C^2 m} \right) \lambda_1^4 \eta_1^2.$$

Taking $\lambda_1, \lambda_2 \ldots$ in order of diminishing magnitude, we may write

$$\frac{\lambda^2}{\lambda^2 - \lambda_2^2} \lambda_2^2 \eta_2 = \alpha \frac{\lambda^2}{\lambda^2 - \lambda_1^2} \lambda_1^2 \eta_1,$$

$$\frac{\lambda^2}{\lambda^2 - \lambda_3^2} \lambda_3^2 \eta_3 = \beta \frac{\lambda^2}{\lambda^2 - \lambda_1^2} \lambda_1^2 \eta_1, \text{ \&c.}$$

Unless η varies more rapidly than the inverse square of the dispersional period, α_1, $\beta_1 \ldots$ will be all less than unity.
Thus

$$n^2 - 1 - a_0 = \frac{e^2}{\pi C^2 m} \lambda_1{}^2 \eta_1 \left(\frac{\lambda^2}{\lambda^2 - \lambda_1{}^2}\right) [N_1 + N_2 \alpha + N_3 \beta + \ldots]$$

$$\phi = \frac{1}{e} \frac{\pi}{2} \cdot \left(\frac{e^2}{\pi C^2 m}\right)^2 \lambda_1{}^4 \eta_1{}^2 \left(\frac{\lambda^2}{\lambda^2 - \lambda_1{}^2}\right)^2 [N_1 + N_2 \alpha^2 + N_3 \beta^2 + \ldots].$$

Hence

$$\frac{(n^2 - 1 - a_0)^2}{\phi} = \frac{2e}{\pi} \frac{[N_1 + N_2 \alpha + N_3 \beta + \ldots]^2}{N_1 + N_2 \alpha^2 + N_3 \beta^2 + \ldots} \cdot \quad \cdot \quad \cdot \quad (\delta)$$

$$= \frac{2e}{\pi} N'.$$

In applying this formula we may note that *—

(i.) $N' > N_1$. Hence the result will furnish an upper limit to the number of electrons of the longest ultra-violet period.

(ii.) When λ_1, $\lambda_2 \ldots$ are not widely separated, N' approximates closely to $(N_1 + N_2 + N_3 + \ldots)$, and the result gives the total number of *dispersional* electrons very nearly.

(iii.) As a_0 is known for very few substances, it must usually be neglected and the result treated as an augmented value of p. When condition (ii.) is satisfied, the result will be a close approximation to the *total* number of *refractive* electrons †.

(iv.) In the case of unsaturated compounds, the value of N' will be influenced by the small values of α, β, etc.

Using equation (1) to find the number of electrons per molecule, we have

$$p = \frac{\pi}{2} \cdot \frac{(n^2 - 1 - a_0)^2}{\phi} \cdot \frac{M}{d} \cdot \frac{1}{e/h}. \quad \cdot \quad \cdot \quad (9)$$

Denoting the specific rotation and molecular rotation relative to water by ρ and R_w respectively, we obtain

$$\rho = \frac{\delta}{\cdot 01308 \times \cdot 0002909} \text{ for } \lambda = \cdot 5893 \, \mu,$$

$$p = \frac{(n^2 - 1 - a_0)^2}{n} \cdot \frac{M}{d\rho} \times \cdot 4105, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

and $$p = \frac{(n^2 - 1 - a_0)^2}{n} \cdot \frac{M^2}{R_w d^2} \times \cdot 02285. \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

* See Note 1.
† *Cf.* results for aliphatic compounds, Table III.

The expression for p obtained from natural dispersion contains e/m, but it will be noticed that this quantity is eliminated in the present calculation.

The values of p for some typical organic substances calculated from equations (10) or (11) are given in Table III., a_0 and ζ being in all cases neglected. Normal values of v only are given.

TABLE III.

Substance.	v.	ρ_D.	$_D R_w$.	p_1 (min.).
Water	4	1	...	3·4
Carbon bisulphide	8	3·3	...	12·5
Methyl alcohol	10	...	1·64	10·0
Ethyl alcohol	16	...	2·78	14·6
n. Propyl alcohol	22	...	3·768	20·5
Amyl alcohol	34	·989	...	31·0
Acetaldehyde	14	...	2·385	13·6
Propaldehyde	20	...	3·332	19·1
Acetone	20	...	3·514	18·3
Formic acid	10	...	1·671	11·0
Acetic acid	16	..	2·525	16·7
Propionic acid	22	...	3·462	22·3
Butyric acid	28	...	4·472	27·9
Valerianic acid	34	...	5·513	33·4
Œnanthylic acid	46	...	7·552	44·5
Methyl acetate	22	...	3·362	24·2
Ethyl acetate	28	...	4·462	27·7
Propyl acetate..............	34	...	5·487	33·4
Hexane	38	...	6·670	33·5
Benzene	30	2·305	...	16·6
Orthoxylene	42	1·989	...	27·3
Diphenylmethane............	64	2·560	...	33·2
Triphenylmethane	92	2·770	...	49·5
Diphenyl	58	2·940	...	29·7
Dimethylorthotoluidine ...	52	2·316	...	29·6
Dimethylparatoluidine ...	52	2·869	...	25·9
Indene	44	2·448	...	27·8
Hydrindene	46	2·040	...	30·1
Orthotolylmethyloxide ...	44	2·208	...	26·2
Dimethylresorcinol	46	2·095	...	29·4
Metaguaiacol	40	2·428	...	22·3
a-naphthylethyloxide	62	3·588	...	27·7
β- ,, ,, ...	62	3·336	...	28·5
Ethylic anisate	58	1·914	...	40·9
m. Phenylenediamine	38	3·576	...	18·7
Dimethyl-*β*-naphthylamine	64	5·144	...	23·2
a-monobromnaphthalin ...	48	3·826	...	27·1

A comparison of the columns v and p shows that probably in every case the number of electrons influencing the refraction is not greater than the total number of normal valencies of the atoms.

The value of a_0 is known fairly accurately for the few substances whose dispersions have been measured over a large range of wave-lengths. Thus for quartz, fluorite, sylvine, and rock-salt we have $a_0 = \cdot 37$, $\cdot 35$, $\cdot 25$, $\cdot 19$ respectively, and the values of p calculated from (10) as given below.

TABLE IV.

Substance.	δ (minutes).	M.	d.	n_D.	p.
Quartz	$\cdot 01664$	$60\cdot4$	$2\cdot65$	$1\cdot5443$	$4\cdot9$
Fluorite	$\cdot 00897$	$78\cdot0$	$3\cdot18$	$1\cdot4339$	$5\cdot10$
Rock-salt	$\cdot 03280$	$58\cdot5$	$2\cdot15$	$1\cdot5443$	$4\cdot12$
Sylvine	$\cdot 02670$	$74\cdot6$	$1\cdot95$	$1\cdot4904$	$4\cdot87$

In fluorite, rock-salt, and sylvine, Meyer [*] finds that the fundamental formula

$$\delta = \frac{e}{2mC^2} \lambda \frac{dn}{d\lambda} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

agrees well with the experimental results when n does not involve infra-red influences. Hence for these substances the dispersional period in the ultraviolet deduced from magnetic rotation should agree with that deduced from dispersion, and if more than one period is involved the effective e/m is therefore the same for both. Introducing η as above $(\eta_1 = \eta_2 = \eta)$, Meyer's results give for

Fluorite .... $\eta \dfrac{e}{m} = 1\cdot 21 \times 10^7$ (e.m.u.)

Rock-salt .... ,, $= 1\cdot 51$

Sylvine .... ,, $= 1\cdot 42$.

The magnetic dispersion in quartz in the visible spectrum has been subjected to very accurate investigation by Lowry [†]. Taking the relative values obtained for $\cdot 6708\,\mu$ and $\cdot 4800\,\mu$ near the ends of the visible spectrum, namely, $\cdot 646$ and $1\cdot 318$, with $n = 1\cdot 5415$ and $1\cdot 5501$ respectively, and using equation (9) (Part I.), we obtain

$$\lambda_1 = \cdot 106\,\mu.$$

The period thus deduced from the magnetic effect agrees

[*] *Ann. d. Phys.* (30) p. 607 (1909).
[†] Phil. Trans. A. vol. ccxii. p. 295 (1913).

very closely with that obtained by Rubens from natural dispersion, namely,

$$\lambda_1 = \cdot 103 \, \mu.$$

Hence we may conclude that only one value of η occurs here. For this substance Rubens gives $a_1\lambda_1{}^2 = \cdot 010654$. Substituting these values in equation (12), and taking $\delta = \cdot 01664'$ for $\lambda = \cdot 5893$, I find

$$\eta \frac{e}{m} = 1 \cdot 37 \times 10^7 \text{ e.m.u.}$$

If the values of the effective e/m thus determined are used in place of the normal value for calculating the value of p from the natural dispersion (Table II.), we obtain [*]:—

Quartz ...... $p = 5 \cdot 1$,   Sylvine ...... $p = 2 \cdot 4$,

Fluorite...... $p = 5 \cdot 1$,   Rock-salt ... $p = 4 \cdot 2$.

For other substances the value of a_0 is not known with the same degree of certainty, since the determinations of n have not been made with sufficient accuracy over a large range of the spectrum. Taking the values at present obtained, the results for several liquids are given below, equation (10) being used.

TABLE V.

Substance.	ρ.	d.	n_{D}.	a_0.	p.
Water	1	1	1·333	·268	1·4
Carbon-bisulphide	3·250	1·263	1·6307	·634	4·9
Benzene	2·305	·879	1·5005	·557	5·1
m. Xylene	1·896	·878	1·4950	·614	6·7
Naphthalene bromide	3·826	1·487	1·6582	·954	5·7

It will be noticed that the values of p in comparison with v are always much smaller in unsaturated compounds than in others. This is in all probability due to the existence of a long dispersional period widely separated from the next shorter period.

The calculation of p from the formula for magnetic rotation alone could be made if the constants were known. From the formulæ obtained in Part I. for some of the above

liquids * we may calculate the number of electrons of longest period in terms of η and $(1+\zeta)$, since

$$k_1 = (1+\zeta)\eta_1{}^2 \frac{\lambda_1{}^4}{2\pi C^2} \left(\frac{e}{m}\right)^2 N_1 e.$$

Neglecting ζ, we obtain:—

Water...... $p_1\eta_1{}^2 = \cdot296,$ m. Xylene ... $p_1\eta_1{}^2 = 1\cdot176,$
Benzene... $p_1\eta_1{}^2 = 1\cdot038,$ Naph. brom. .. $p_1\eta_1{}^2 = \cdot625.$

As λ_1 enters to the fourth power, a small error in its value will considerably affect the result.

The above numerical results may now be reviewed in connexion with the electronic theory of valency. According to the electrostatic theory of J. J. Thomson and Ramsay, the force of chemical affinity is produced by the transference of a negative electron from one atom to another; in that of Stark the electron is attached to neither atom but exerts an attraction on both; whilst in the hypothesis recently put forward by Arsem [†], the particle is in a state of continual oscillation from one atom to the other. Without, however, formulating any hypothesis as to the mechanism by which the electron sets up the force of chemical affinity, whether electrostatic or electromagnetic, we may conclude that only one electron is concerned in the production of each " bond " of affinity; and the theory of J. J. Thomson and Ramsay may be used as the most convenient way of distinguishing between these electrons and others associated with the atom. Remembering that the molecule as a whole is neutral and commencing with the atoms of which it is composed assembled in their neutral state, it is clear that the number of electrons to be transferred is equal to the number of active positive valencies in the molecule. Now according to the theory of Abegg [‡], these will represent either normal or contravalencies according to the group of the periodic system in which the element falls. Thus, for example, we have:

Group	1	2	3	4	5	6	7	0
Element ...	Na	Mg	Al	Si	P	S	Cl	A
+ Valency...	+1	+2	+3	+4	+5	+6	+7	0

Normal.   Contra.

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* In the tables given in Part I. for naphthalene bromide and carbon bisulphide, the values given under δ are those of $n\delta$.
† Jour. Amer. Chem. Soc. (36) pp. 1655–1675 (Aug. 1914).
‡ *Zeit. anorg. Chem.* (39) p. 330 (1904).

Hence the sum of such values for the atoms present in a molecule gives the maximum number of electrons capable of producing affinity; and this number should be taken for v in place of the normal valencies. The numbers in parenthesis given under v in the tables are calculated in this way.

It is to be expected that the electrons which produce the attraction between the atoms in a given compound, and which according to Thomson's theory are transferred from one atom to the other, will be those subjected to the weakest controlling forces and will be, therefore, the long-period electrons which give rise to the dispersion and magnetic rotation. Various considerations support this view. When the number of bonds increases relatively to the number of atoms, as in unsaturated and aromatic compounds, the dispersive power undergoes a marked exaltation. The numerical values obtained above for the upper limit to the number of electrons of longest period are too small to be associated with any but the active bonds. In quartz, where the dispersion constants are probably more accurately known than in the case of any other substance, we have $p_1 = 4$, *i.e.* one electron for each bond in the molecule. In elements, however, which show high positive contravalency, particularly those of high atomic weight, the electrons not associated with the bonds may influence the dispersion owing to weak controlling forces. Thus the six contravalency electrons of sulphur are probably responsible for a large part of the dispersion and refraction in carbon bisulphide, and the same is probably true of nitrogen in the highly refractive amines. The point of view assumed in the present theory will perhaps be rendered more definite if we make a distinction between the various electrons which may influence the optical properties as follows.

Class I. The recent application of photometrical measurements to absorption phenomena has shown that the characteristic absorption bands in many cases must be attributed to electrons whose number in the unit of volume is only a small fraction of the number of molecules. Henri [*] finds the absorption in acetone is produced by 1 resonator in 36 molecules; Baly and Tryhorn [†] find the number of molecules operating in the production of the less refrangible aniline band is 1 in 30; Kœnigsberger and Kilchling [‡] deduce for the bromine band at ·412 μ only 1 in 60. Hallo, from observations on the magnetic rotation in sodium vapour,

[*] *Phys. Zeit.* (14) p. 515 (1913).
[†] Trans. Chem. Soc. (107) p. 1121 (1915).
[‡] *Ann. d. Phys.* (28) p. 889 (1909).

obtains an exceedingly small fraction for the ratio of the effective to the total number of molecules. It appears that the frequency brought into play in these cases is due to some accidental or seldom-recurring condition of the molecule. On account of their small number, electrons of this type have little influence on the refractive index or magnetic rotation, except quite close to the absorption band to which they give rise, but are probably capable of giving rise to fluorescence and phosphorescence.

Class II. Valency electrons of dispersional type :—

(a) Under this heading are included the electrons through whose agency the attraction between the atoms in any given molecule is produced. Every such particle represents *one* valency bond.

(b) The contravalency electrons of certain elements, particularly N, P, S, Cl, Br, I, may have a frequency sufficiently low to affect the dispersion as well as the refraction. This is more marked in the case of the elements which readily part with these electrons, *e. g.* sulphur and iodine.

Class III. Valency electrons of non-dispersional type.— These differ from class II. in possessing a frequency so high that their effect on the dispersion cannot be detected experimentally, whilst they still exert a measurable influence on the refraction.

Class IV. Intra-atomic electrons.—This term may be used for referring to electrons present in the atom which take no part in deciding the valency. Such electrons will undergo so little displacement relative to their positive complement, that it is probable that each will exert only a very small effect on the refraction.

An examination of the numerical values given in the preceding tables shows the following relations hold good :—

(a) The *minimum* number of electrons demanded by the *refraction* calculated on the normal value of e/m is never greater than the total number of positive (normal or contra-) valency electrons ; it is never greater than the sum of those of class II. and class III.

(b) The *minimum* number allowed by the dispersion and magnetic rotation is never greater than the sum of those of classes II. (a) and II. (b).

(c) The *maximum* number of electrons of the longest period allowed by the dispersion and magnetic rotation is never greater than the number of electrons of class II.

The empirical character of the four-constant formula

$$n^2-1=a_0+\frac{a_1\lambda^2}{\lambda^2-\lambda_1^2}-c\lambda^2$$

has already been referred to. When there are more dispersional periods than one, the shorter ones are more likely to escape detection than the longer and the tendency is to obtain too great a value for λ_1, with the result that a_1 is too small and a_0 too great. The accuracy with which the constants can be determined depends of course upon the range of spectrum covered by the observations and upon the accuracy with which the individual values of n have been determined. Where both conditions have been fulfilled, as in the case of quartz, rock-salt, sylvine, and fluorspar, the value obtained for a_0 is always a small fraction.

In a homologous series of organic compounds each addition of a methylene group adds an equal number of electrons to the molecule, but as such addition also produces an approximately constant increment in the molecular volume, the number of electrons in the unit of volume or the quantity p/V_m tends towards a constant value as we proceed to the higher members of the series. As this applies to the electrons of each class independently (except class I.) we ought to find that the value of a_0 which depends upon the number of electrons of class III. (possibly also to a slight extent of class IV.) in the unit volume approximates to a constant value. The following table shows that numerical results are quite in accordance with this view. p_1 is put equal to the number of linkages (class II. a) and a_0 is calculated from equation (11). As the compounds are aliphatic condition (ii.) is satisfied.

TABLE VI.

Substance.	p_1.	a_0.	Substance.	p_1.	a_0.
Pentane	16	·206	Formic acid	5	·286
Hexane	19	·220	Acetic acid	8	·271
Octane	25	·233	Propionic acid	11	·275
Methyl alcohol	5	·223	Butyric acid	14	·278
Ethyl alcohol	8	·221	Valerianic acid	17	·279
n. Propyl alcohol	11	·246	Œnanthylic acid	23	·287
Acetaldehyde	7	·219	Methyl acetate	11	·277
Propaldehyde	10	·238	Ethyl acetate	14	·255
Acetone	10	·222	Propyl acetate	17	·262

In view of the fact that N', equation (8), is only an approximation to $N_1 + N_2 + N_3 + \ldots$ the uniformity in the values of a_0 is even greater than might have been expected[*].

In the following section we proceed to consider the bearing of the present theory on the additive optical properties of organic substances.

[*] See Note 3.

The Correlation of Additive Properties in Magnetic Rotation and Refraction.

In seeking to obtain additive relations between the optical properties of a substance, it is necessary to bear in mind that the electrons associated with the atom of a given element will possess different periods in different substances. The polarization of the medium set up by the electric force of the light-wave which, if averaged or smoothed-out would be neutralized by the polar field of the medium as a whole, owing to the discontinuous structure of matter, is locally concentrated in the vicinity of the individual molecules. The polarization near the molecules therefore exceeds the polar field, and the excess constitutes a force acting on the electron in opposition to the controlling force exerted by the atom. The period of the electron is thus increased, and must be distinguished from the period which the electron would have if the atom were isolated. The degree of augmentation, since it depends upon the degree of polarization, will vary with the nature and density of the substance. Any term of the dispersion formula which represents the effect of the electrons of a given kind of atom will possess different constants in respect of different substances. This of course applies equally to magnetic rotation. In order that the dispersion formulæ for different substances may all contain the same term for the electrons of a given kind of atom, it is necessary to eliminate the polarization effect and to obtain a summational expression in terms of the *isolation* frequencies of the resonators. Whilst the necessity for doing this has been generally recognized in the case of refraction, it is noteworthy that, with regard to the magnetic rotation, additive relations have been sought for always from the values of this quantity as directly measured. The influence of polarization on refraction has been fully investigated by H. A. Lorentz, and the components of molecular refraction are usually determined from the well-known Lorenz-Lorentz formula. The results are more consistent than those obtained from magnetic rotation, and the latter quantity has therefore been regarded as more highly constitutive than refraction. Whilst this may be quite true, it is clear that polarization effects should be eliminated in the magnetic case and the contribution of each electron expressed in terms of the isolation frequency of that electron.

Lorentz [*] deduces an expression for the rotation which,

* 'Theory of Electrons,' p. 163, eqn. (246).

using δ for this quantity, may be written

$$\delta = \frac{\nu}{4\mathrm{C}} \left\{ \frac{\alpha + \gamma}{(\alpha + \gamma)^2 + \beta^2} - \frac{\alpha - \gamma}{(\alpha - \gamma)^2 + \beta^2} \right\},$$

where ν is the frequency (angular velocity) of the incident light, and putting ν_0 for the angular velocity of an electron vibrating with its isolation frequency, and a for the polarization constant,

$$\alpha = \frac{m}{\mathrm{N}e^2}(\nu_0{}^2 - \nu^2) - a \;;$$

$$\beta = \frac{\nu g}{\mathrm{N}e^2}\;; \qquad \gamma = \frac{\nu \mathrm{H}}{\mathrm{C}\mathrm{N}e}.$$

A more convenient expression has been obtained by G. H. Livens [*] which, in terms of the symbols used in the preceding parts of this paper, becomes

$$n_{\pm}^2 - 1 = \frac{\Sigma \dfrac{e^2}{m_1(\nu_1{}^2 - \nu^2) \mp \dfrac{e\nu\mathrm{H}}{\mathrm{C}}}}{1 - \Sigma \dfrac{ae^2}{m(\nu_1{}^2 - \nu^2) \mp \dfrac{e\nu\mathrm{H}}{\mathrm{C}}}},$$

in which the $+$ and $-$ suffixes distinguish the values of n for circularly polarized light of opposite chiralities.

Since

$$\delta = \frac{\nu}{4n\mathrm{C}}(n_-^2 - n_+^2),$$

we have

$$\delta_{\mathrm{H}} = \frac{e\mathrm{H}\nu^2}{2n\mathrm{C}^2} \frac{\Sigma \dfrac{e^2}{m_1{}^2(\nu_1{}^2 - \nu^2)^2}}{\left(1 - \Sigma \dfrac{ae^2}{m_1(\nu_1{}^2 - \nu^2)}\right)^2}.$$

Taking the polarization constant a as $1/3$ and writing

$$\Sigma \frac{e^2}{m(\nu_1{}^2 - \nu^2) \mp \dfrac{e\nu\mathrm{H}}{\mathrm{C}}} = \omega_{\mp},$$

we obtain

$$n_{\pm}^2 - 1 = \frac{\omega_{\mp}}{1 - \dfrac{1}{3}\omega_{\mp}}\;; \quad n_{\pm}^2 + 2 = \frac{3}{1 - \dfrac{\omega_{\mp}}{3}}.$$

[*] Phil. Mag. August 1913, p. 362.

Hence

$$n_-^2 - n_+^2 = \frac{\omega_+}{1 - \frac{\omega_+}{3}} - \frac{\omega_-}{1 - \frac{\omega_-}{3}}$$

$$= \frac{\omega_+ - \omega_-}{\left(1 - \frac{\omega}{3}\right)^2}$$

$$= \left(\frac{n^2 + 2}{3}\right)^2 (\omega_+ - \omega_-).$$

Now

$$\omega_+ = \frac{e^2}{m_1(\nu_1^2 - \nu^2) + \frac{e\nu H}{C}} + \ldots\ldots\ldots$$

$$\omega_- = \frac{e^2}{m_1(\nu_1^2 - \nu^2) - \frac{e\nu H}{C}} + \ldots\ldots\ldots$$

Therefore

$$\omega_+ - \omega_- = -\left[\epsilon^2 \cdot \frac{2e\nu H}{C} \cdot \frac{1}{m_1^2(\nu_1^2 - \nu^2)^2 - \left(\frac{e\nu H}{C}\right)^2} + \ldots\right]$$

$$= -\frac{2e^3\nu H}{C}\left[\frac{1}{m_1^2(\nu_1^2 - \nu^2)^2} + \ldots\right],$$

on account of the relatively small value of $(e\nu H/C)^2$.

Thus

$$n_-^2 - n_+^2 = -\left(\frac{n^2 + 2}{3}\right)^2 \cdot \frac{2\nu H}{C} \cdot \Sigma \frac{e^3}{m_1^2(\nu_1^2 - \nu^2)^2}$$

and

$$\delta_H = -\frac{\nu}{4nC} \cdot \left(\frac{n^2 + 2}{3}\right)^2 \cdot \frac{2\nu H}{C} \Sigma \frac{e^3}{m_1^2(\nu_1^2 - \nu^2)^2}$$

$$= -\frac{\nu^2 H}{2nC^2}\left(\frac{n^2 + 2}{3}\right)^2 \Sigma \frac{e^3}{m_1^2(\nu_1^2 - \nu^2)^2}$$

$$= -\frac{\nu^2 H}{2nC^2}\left(\frac{n^2 + 2}{3}\right)^2 \Sigma \left\{\frac{e^2}{m_1(\nu_1^2 - \nu^2)}\right\}^2 \frac{1}{e}.$$

But from Lorentz's expression for the component of the refraction [*], we may put for the effect of each electron

$$\frac{n_1^2 - 1}{n_1^2 + 2} = \frac{1}{3}\frac{e^2}{m_1(\nu_1^2 - \nu^2)}.$$

[*] 'Theory of Electrons,' Note 58, p. 308.

Hence

$$\delta_H = - \frac{\nu^2 H}{2nC^2}(n^2+2)^2 \Sigma\left(\frac{n_1^2-1}{n_1^2+2}\right)^2 \cdot \frac{1}{e}.$$

Converting from rational to ordinary symmetrical units and taking ν in periods per second, we must write

$$\frac{H}{\sqrt{4\pi}} \text{ for H, } e\sqrt{4\pi} \text{ for } e, \text{ and } 2\pi\nu \text{ for } \nu.$$

Thus

$$\delta_H = \frac{\pi\nu^2 H}{2C^2 e} \cdot \frac{(n^2+2)^2}{n} \Sigma\left(\frac{n_1^2-1}{n_2^2+2}\right)^2.$$

The summation here extends to all the electrons in the unit of volume; but as every type of electron present in one molecule is repeated in every molecule (except those of class I. which do not produce a measurable effect) we may write

$$\delta_H = \frac{\pi\nu^2 H}{2C^2 e} \cdot \frac{(n^2+2)^2}{n} \left\{ N\left(\frac{n_1^2-1}{n_1^2+2}\right)^2 + \ldots + N\left(\frac{n_p^2-1}{n_p^2+2}\right) \right\}^2,$$

where N is now the number of molecules in the unit of volume, and the summation extends to the p individual effective electrons in the molecule. The components of the molecular refraction as usually calculated with the same notation are expressed in

$$\frac{n^2-1}{n^2+2}\frac{M}{d} = \left(N\frac{n_1^2-1}{n_1^2+2}\right)\frac{M}{d} + \ldots \text{ to } p \text{ terms,}$$
$$= P_1 + P_2 + \ldots\ldots + P_p.$$

The expression for the absolute molecular rotation R $(=M\delta/d)$ may therefore be written

$$R = \frac{\pi\nu^2}{2C^2 e}\frac{(n^2+2)^2}{n} \cdot \frac{d}{NM}\{P_1^2 + P_2^2 + \ldots + P_p^2\}.$$

But since $N = d/Mh$ this becomes

$$R = \frac{\pi\nu^2}{2C^2 e/h}\frac{(n^2+2)^2}{n} \cdot \{P_1^2 + P_2^2 + \ldots + P_p^2\}. \quad . \quad (1)$$

Hence the quantity in which we must seek the additive relations is not the molecular rotation R simply *, but

$$R\frac{n}{(n^2+2)^2}.$$

* See Note 4.

The magnetic rotation is usually measured for the sodium line, and the molecular rotation generally recorded is not the absolute molecular rotation but the ratio of this quantity to the corresponding quantity for water. Calling the ratio R_w and substituting the usual numerical values of the constants, we have

$$R_w \frac{n}{(n^2+2)^2} \times 43 \cdot 748 = \{ P_1^2 + P_2^2 + \ldots + P_p^2 \}, \quad (2)$$

in which the molecular rotation is expressed in terms of the molecular refraction components.

According to the theory put forward above, only the electrons of class II. (a) or II. (b) influence the dispersion and magnetic rotation. In general, where the resonators II. (b) are not operative, the number of terms in the summation will depend on the number of bonds only, and the value of P for each bond may be calculated. Using the notation (CC), (CH), to denote the value of P for the electron concerned in each linkage respectively, we may deduce the numerical values as follows.

Taking the two hydrocarbons pentane and hexane, for example, we have by experiment,

For hexane .... $R_w = 6\cdot670,$ $n_D = 1\cdot3754$;

For pentane .... $R_w = 5\cdot658,$ $n_D = 1\cdot3581.$

Substituting these values in (2),

$$26\cdot50 \ = 5(CC)^2 + 14(CH)^2 \ \text{(hexane)},$$
$$22\cdot665 = 4(CC)^2 + 12(CH)^2 \ \text{(pentane)},$$

whence

$$(CH)^2 = 1\cdot831, \qquad (CC)^2 \doteqdot \cdot172.$$

On account of the approximate constancy of the differences for a CH_2 group, only two independent equations can be obtained from a homologous series. Hence we cannot obtain evidence from equation (2) of the null effect of electrons of classes III. and IV., and for the present must rely on the considerations already given. Numerical confirmation will be obtained when we come to the calculation of refraction for the alcohols.

For the value of the CO linkage we may consider one of the ethers. Selecting ethyl ether,

$$R_w = 4\cdot800, \quad n_D = 1\cdot3566,$$
$$19\cdot315 = 2(CC)^2 + 10(CH)^2 + 2(CO)^2,$$

whence $(CO)^2 = \cdot3305.$

Selecting *n.* propyl alcohol for the determination of the value of (OH), we have

$$R_w = 3\cdot768, \quad n_D = 1\cdot3854,$$
$$14\cdot867 = 2(CC)^2 + 7(CH)^2 + (CO)^2 + (OH)^2,$$

whence

$$(OH)^2 = 1\cdot376.$$

In the case of the carbonyl group we cannot separate the values of P for the two linkages, and can only determine the sum of the squares. In this and other cases of unsaturation the summation may be indicated by prefixing Σ.

Choosing propionic acid for this,

$$R_w = 3\cdot462, \quad n_D = 1\cdot3866,$$
$$13\cdot648 = 2(CC)^2 + 5(CH)^2 + (CO)^2 + (OH)^2 + \Sigma(CO)^2,$$

which gives

$$\Sigma(CO)^2 = 2\cdot443.$$

Using the above values we may calculate the value of R_w, if the value of n_D is known, for organic compounds involving only these linkages.

TABLE VII.

Substance.	n_D.	R_w (obs.).	R_w (calc.).	Diff.
Pentane	1·3581	5·638	5·638	ref.
Hexane	1·3754	6·670	6·670	ref.
Octane	1·3963	8·722	8·724	+·002
Methyl alcohol	1·3294	1·640	1·757	+·117
Ethyl alcohol	1·3623	2·780	2·752	−·028
n. Propyl alcohol	1·3854	3·768	3·768	ref.
n. Butyl alcohol	1·3991	4·760	4·785	+·025
Glycerine	1·4729	4·093	3·944	−·149
Ethyl ether	1·3529	4·799	4·799	ref.
Formic acid	1·3714	1·671	1·501	−·170
Acetic acid	1·3718	2·525	2·464	−·061
Propionic acid	1·3866	3·462	3·462	ref.
Butyric acid	1·3979	4·472	4·469	−·003
Valerianic acid..............	1·4043	5·513	5·474	−·039
Œnanthylic acid	1·4215	7·552	7·534	−·018
i. Butyric acid	1·3930	4·444	4·454	+·010
Acetaldehyde	1·3316	2·385	2·429	+·044
Propaldehyde	1·3636	3·332	3·439	+·107
Acetone	1·3591	3·514	3·428	−·086
Methyl acetate	1·3610	3·362	3·555	+·193
Methyl butyrate	1·3889	5·374	5·571	+·197
Ethyl formate	1·3598	3·551	3·552	+·001
Ethyl acetate	1·3726	4·462	4·546	+·084
Ethyl butyrate	1·3960	6·477	6·580	+·103
Ethyl valeriate	1·3970	7·500	7·562	+·062
Ethyl oxalate	1·4104	6·654	6·457	−·197
Propyl acetate	1·3844	5·487	5·554	+·067

The values of n_D are those of Conrady, and R_w is that of Perkin.

It will be seen that although the values of the linkages are those deduced from R_w for a single substance in each case, no attempt being made to work out mean values, a very fair agreement between the observed and calculated values is obtained.

Turning now to the refraction, we have

$$P = \left(\frac{n^2-1}{n^2+2}\right)\frac{M}{d} = P_1 + P_2 + \ldots + P_p.$$

The values of P_1^2, &c. given by the magnetic rotation for the linkages (CC), (CH), CO), (OH) enable us to calculate at once the corresponding values of P.

$$(CH) = 1\cdot353, \qquad (CO) = \cdot574,$$
$$(CC) = \cdot415, \qquad (OH) = 1\cdot173.$$

The sum of the P's for the electrons of classes III. and IV. of the atoms C, H, O must first be calculated, for which we may use the following values for the molecular refractive power with reference to the D line.

$$\begin{aligned}
&\text{Pentane} \quad \ldots\ldots\ldots \quad P = 25\cdot17\\
&\text{Hexane} \ldots\ldots\ldots\ldots \quad P = 29\cdot71\\
&\text{Ether} \ldots\ldots\ldots\ldots\ldots \quad P = 22\cdot37
\end{aligned}$$

Thus denoting the sums just referred to by the symbols C, H, and O, we have

$$\begin{aligned}
29\cdot71 &= 5(CC) + 14(CH) + 6C + 14H\\
&= 21\cdot015 + 6C + 14H,\\
25\cdot17 &= 4(CC) + 12(CH) + 5C + 12H\\
&= 17\cdot895 + 5C + 12H,
\end{aligned}$$

whence $\qquad H = \cdot087, \qquad C = 1\cdot245.$

For the oxygen atom,

$$22\cdot37 = 2(CC) + 10(CH) + 2(CO) + 4C + 10H + O.$$

Hence $\qquad\qquad O = 1\cdot013.$

The two linkages of the carbonyl group cannot be evaluated from the magnetic rotation, since the latter gives the sum of the squares of the two P's, and these may not be of equal value. We must obtain $\Sigma(CO)$ therefore from the

refraction. Taking propionic acid, for which $P = 17·46$, we have

$$17·46 = 2(CC) + 5(CH) + (CO) + (OH) + \Sigma(CO) + 3C + 6H + 2O$$
$$= ·829 + 6·765 + ·574 + 1·173 + \Sigma(CO) + 3·735 + ·522 + 2·026$$

whence $\Sigma(CO) = 1·836$.

The additive relations between the refractive powers or the magnetic rotations deduced by the methods of Landolt, Brühl, and Perkin, rest *solely* on the constancy of the difference introduced by the addition of the group $—CH_2—$ in different series of homologous compounds. But we must note it is perfectly arbitrary whether the summation shall be referred to the atoms alone, as in the usual theory, or to the valency linkages alone [*], or to the two combined as in the present theory. For this theory it may be claimed (1) that it contains internal evidence of its truth, (2) the values obtained admit of a more rational interpretation than those of the "atomic" method, (3) it correlates the phenomena of magnetic rotation and refraction.

The test referred to in (1) is provided by the alcohols. The value of the (OH) linkage may be determined from the molecular rotation, or independently from the refraction. For the latter, taking propyl alcohol, we have $P = 17·46$, and therefore

$$17·46 = 2(CC) + 7(CH) + (CO) + (OH) + 3C + 8H + O$$
$$= 16·319 + OH ;$$

whence $OH = 1·141$.

The value of OH deduced from the magnetic rotation of propyl alcohol is $1·173$, a sufficiently close agreement. The mean value of OH deduced from the refraction of six alcohols is $1·136$.

With regard to (2) it may be remarked that the small values of the (CC) and (CO) linkages indicate higher frequencies and therefore stronger controlling forces on the electrons, than in the (CH) and (OH) linkages. This result may reasonably be associated with the more easily replaceable character of the H atoms in the latter. Further, the atomic value for H is very small ($·087$), which accords with its

---

[*] In terms of the linkages alone I find the following values for the components of the molecular refraction for the H_α line :—

$(CH) = 1·683$, $(CC) = 1·249$, $(CO) = 1·493$, $(OH) = 1·627$, $(C = O) = 3·404$. Thus for ethyl alcohol : $P_\alpha = 5(CH) + (CC) + (CO) + (OH)$
$$= 12·78. \quad \text{(Observed value 12·71.)}$$

small atomic weight and low valency. The refractive effect of H is probably due entirely to electrons of class IV. The values obtained by the ordinary " atomic " method do not admit of any such interpretation, the value for H being 1·05 and that for C, an atom of 12 times the atomic weight and 4 times the valency, being only 2·5.

The subjoined table gives the values of P for a number of aliphatic compounds calculated from

$$
\begin{aligned}
(CC) &= \cdot 415 & C &= 1\cdot 245 \\
(CH) &= 1\cdot 353 & H &= \cdot 087 \\
(CO) &= \cdot 574 & O &= 1\cdot 013 \\
(OH) &= 1\cdot 173 \\
\Sigma(CO) &= 1\cdot 836
\end{aligned}
$$

TABLE VIII.

Substance.	P (obs.).	P (calc.).	Diff.
Pentane	25·17	25·17	ref.
Hexane	29·71	29·71	ref.
Octane	38·70	38·78	+·08
Methyl alcohol	8·25	8·41	+·16
Ethyl alcohol	12·74	12·95	+·21
Propyl alcohol	17·46	17·49	+·03
n. Butyl alcohol	22·06	22·03	−·03
Glycerine	20·45	20·31	−·14
Ethyl ether	22·37	22·37	ref.
Propyl-ethyl ether	26·86	26·91	+·05
Formic acid	8·54	8·38	−·16
Acetic acid	12·96	12·92	−·04
Propionic acid	17·46	17·46	ref.
Butyric acid	22·10	22·00	−·10
Valerianic acid	26·79	26·54	−·25
Caprylic acid	31·30	31·08	−·22
Œnanthylic acid	35·94	35·62	−·32
l. Butyric acid	22·08	22·00	−·08
Acetaldehyde	11·53	11·51	−·02
Propaldehyde	15·97	16·05	+·08
Butyl aldehyde	20·58	20·59	+·01
Valeral	25·38	25·13	−·25
Œnanthol	34·29	34·21	−·08
Acetone	16·09	16·05	−·04
Methyl acetate	18·07	17·80	−·27
Methyl butyrate	26·85	26·88	+·03
Methyl valerate	31·53	31·42	−·11
Ethyl formate	17·97	17·80	−·17
Ethyl acetate	22·18	22·34	+·16
Ethyl butyrate	31·26	31·42	+·16
Ethyl valerate	36·07	35·96	−·11
Ethyl oxalate	33·47	33·13	−·34
n. Propyl acetate	26·89	26·88	−·01
Amyl formate	31·73	31·42	−·31
Amyl valerate	49·83	49·58	−·25

Although the values used were simply deduced from four reference substances, a very fair agreement is shown throughout. A much better agreement may be expected if average values are worked out from a larger number of data, and for some given temperature. Unfortunately, most of the refraction data available have reference to the α line of hydrogen, and the magnetic rotations have reference to the D line. The values of the molecular refraction P in the above table are those of Conrady *, and in many cases were obtained by interpolation.

I hope to deal later with the application of the method to unsaturated and aromatic compounds, and with the recalculation of some of the values given above. If the electrons of class IV. are inoperative, the refractive value of the hydrogen atom in the ultraviolet should be zero. The value ·087 is so small that a better collection of data may prove this to be the case, but the values for the carbon and oxygen atoms can at present only be ascribed to the influence of a large number of electrons of class IV.

Note 1.—From a well-known theorem in inequalities we have for n positive quantities a, b, c, ... k,

$$(a+b+c+ \ldots +k)^2 < n(a^2+b^2+c^2+ \ldots k^2).$$

If now N_1 of the quantities each equal unity, N_2 equal α, &c., we have at once,

$$(N_1+N_2\alpha+N_3\beta+ \ldots)^2 < (N_1+N_2+N_3+ \ldots)(N_1+N_2\alpha^2+N_3\beta^2+ \ldots)$$

Hence, if α, β, &c. are all positive,

$$N' < N_1+N_2+N_3+ \ldots +N_p.$$

Note 2.—In the explanation of the experimental results we have assumed a coefficient η effective in the absence of the magnetic field as well as in its presence, ζ being put zero for simplicity. If, however, the electronic coupling only occurs in the presence of the field, we must write $\eta=1$ and retain ζ. The ratio e/m will then retain its normal value in natural dispersion but not in the magnetic field, and the values of p given in Table II. will hold good.

Note 3.—This result also indicates that the periods of the electrons giving rise to a_0 are approximately the same in the different substances considered, and are therefore little affected by the polarization.

Note 4.—A polarization formula which has only come to my notice since the above has been at press, and which contains the factor $n/(n^2+2)^2$, has been deduced by Sir J. Larmor, with whom

* *Zeits. Phys. Chem.* (3) p. 210 (1899).

therefore rests the priority in calling attention to this point. The formula ('Æther and Matter,' p. 200) gives for the rotation per molecule $(\mu^2+2)^2\eta/9\mu$, where η is a molecular constant proportional to the field. I have also just received through the kindness of Prof. Siertsema a paper on the magnetic rotation in titanium chloride, communicated to the Amsterdam Academy on Oct. 30, 1915, in which he deduces a polarization formula in the form—

$$\chi = \frac{2\nu^2(n^2+2)^2}{9nc} S_{a_1 b_1 \ldots} \frac{D}{(\nu_0^2 - \nu^2)^2}.$$

As the value of D is not given in terms of the electronic constants I am unable to say at present to what extent Prof. Siertsema's formula agrees with that deduced in this paper, except that it clearly supports the use of the factor $n/(n^2+2)^2$.

The George Holt Physics Laboratory,
    University of Liverpool.

LV. *The Absorption of Gases in Vacuum-Tubes, and Allied Phenomena.* By S. BRODETSKY, *M.A., B.Sc., Ph.D., F.R.A.S., Lecturer in Applied Mathematics,* and B. HODGSON, *M.Sc., Ph.D., Assistant Lecturer in Physics, University of Bristol* [*].

1. THE absorption of gases in vacuum-tubes has been the subject of research by many investigators; a satisfactory or unanimous explanation has not, however, been found. The following explanations have been proposed :—

(1) Chemical action between the gas and the glass [1].
(2) Chemical action between the gas and the cathode [2].
(3) Chemical or mechanical action between the gas and the anode [3,4,5].
(4) Chemical action due to active nitrogen [6].
(5) Mechanical occlusion of the gas in the glass [7].
(6) Mechanical occlusion of the gas in the cathode [8].
(7) Mechanical occlusion of the gas in the disintegrated part of the cathode [9].
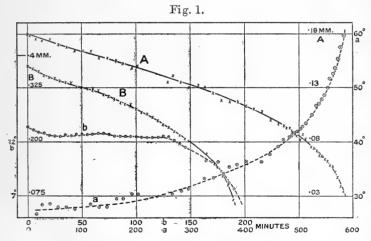
[*] Communicated by the Authors.
[1] Willows, Phil. Mag. i. p. 503 (1901).
[2] Mey, *Ann. d. Phys.* (4) xi. p. 127 (1903).
[3] Skinner, Phil. Mag. xii. p. 481 (1906).
[4] Hodgson, *Phys. Zeit.* xiii. p. 595 (1912).
[5] Chrisler, *Phys. Zeit.* x. p. 745 (1909).
[6] Hill, Proc. Phys. Soc. p. 35 (1912).
[7] Campbell Swinton, Proc. Roy. Soc. lxxix. A, p. 134 (1907).
[8] Riecke, *Ann. d. Phys.* xv. p. 1003 (1904).
[9] Soddy and Mackenzie, Proc. Roy. Soc. lxxx. A, p. 92 (1908).

The results of the experiments to be described in this paper are, on the whole, in agreement with the last explanation.

2. *Apparatus and Method.*—The apparatus and arrangements were similar to those described in Hodgson's paper in the *Physikalische Zeitschrift*[4]. Glass vacuum-tubes were used, and the current was obtained from a high-tension battery. Gas-pressures were read on a McLeod gauge, and voltages on Braun electrometers.

3. *Rate of Absorption compared with Cathode and Anode Temperatures.*—It has been shown that the heat-energy given to the cathode is a function of the cathode-fall[10, 11]. The following experiment was performed to discover whether any relation existed between the temperature of the cathode (a measure of the cathode-fall) and the rate of absorption of the air in a vacuum-tube. A hollow cathode was used, and in it was inserted the bulb of a thermometer. The current was kept constant, and the gas-pressure, cathode temperature, and the time were observed. Curves A, a (in fig. 1) show

Fig. 1.

respectively the pressure-time curve and the temperature-time curve. The curve A is a typical absorption curve for air with copper electrodes. It shows an absorption rate increasing with the time. This means an absorption rate increasing with the cathode-fall, because the latter increases

[4] See par. 1, note 4.
[10] Hodgson and Mainstone, Phil. Mag. xxvi. p. 411 (1913).
[11] Hodgson, Phil. Mag. xxvii. p. 189 (1914).

as the pressure decreases, if the current is kept constant. The temperatures recorded are the excesses above the temperature of the room.

Curves B, b in fig. 1 show the results of a similar experiment when the temperature of the anode was observed. In A the current strength was ·0010 amp., and in B it was ·0040 amp. This accounts for the difference in the slopes of the two absorption-curves. In curve b, it will be seen that the anode temperature actually decreased as the absorption increased. The temperature change in the anode was, however, only small, being 6° C. during the experiment, whilst with the cathode the temperature change was 30° C. for only one quarter the current.

This indicates that the absorption is more related to the cathode than to the anode. It will be seen later, par. 6, that the particular phenomenon associated with the absorption is the disintegration of the cathode [12].
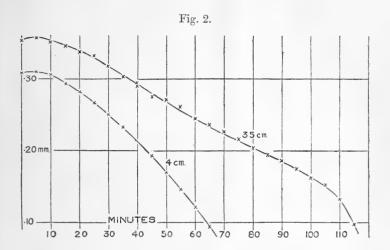
No simple relation could be found between the temperature of the cathode and the rate of absorption. The lag in the reading of the pressure and the temperature made it difficult to approximate closely enough to the actual values. A pressure-gauge *that reads without setting* would be advisable for this work.

4. *Influence of the Length of the Discharge.*—The distance between the electrodes in a vacuum-tube can be increased considerably without altering the conditions at the cathode, if the current strength is kept constant. If the absorption were due to chemical action between the gas and the glass of the tube, then one would expect that the rate of absorption should be greater with a long discharging column than with a short column. One experiment was performed with a distance of 35 cm. between the electrodes, and another with a distance of 4 cm. The results are shown in fig. 2. The absorption curves are similar, the shorter column actually absorbing a little faster than the longer one. Unless we are to suppose that, on the basis of the chemical action theory, the action is confined to a limited region of the glow, the results of these experiments seem to militate against the acceptance of this theory.

5. *Absence of Mechanical Absorption by the Electrodes.*— In order to discover whether there was any mechanical absorption of gas by the electrodes, experiments were performed in which one electrode consisted of a loop of platinum wire that could be raised to a bright heat by

    [12] Tyndall and Hughes, Phil. Mag. xxviii. p. 415 (1914).

means of a current. This electrode was kept at white heat during some hours before an absorption experiment was commenced. During this time, gas was evolved in gradually diminishing quantity : the heating was continued till gas ceased to be evolved.

Fig. 2.

With the platinum loop as cathode an absorption of gas was obtained, the pressure falling from 0·495 to 0·340 mm. On heating the cathode to a white heat, none of the absorbed gas was recovered.

The same was the case with the loop as anode—no absorbed gas was recovered. It is therefore unlikely that the cathode or the anode absorbs gas mechanically.

6. *Experiments with Normal Cathode-Fall.*—Experiments were now performed to see what relation could be found to exist between the rate of absorption and the cathode-fall. With the normal cathode glow—*i. e.* when the cathode glow did not cover the whole of the cathode—practically no absorption was obtained with copper electrodes in air, oxygen, hydrogen, and carbon dioxide. The gas-pressure remained sensibly constant, although currents were passed continuously for long periods. The following table shows the maximum variation of pressure in nineteen experiments.

Now, it was shown by Tyndall and Hughes in the paper already referred to, that there is practically no disintegration

of the cathode with normal cathode-fall.   This suggests, therefore, that there is a close relationship between disintegration and absorption.   Further support is lent to this

Experiments with Normal Cathode-Fall, Copper Electrodes.

Gas used.	Current strength.	Coulombs.	Maximum pressure.	Minimum pressure.
Air	·0080	120	2·79 mm.	2·76 mm.
	·0030	11	2·38	2·365
	·0030	9	1·10	1·06
	·0030	108	2·81	2·77
	·0025	86	2·84	2·80
	·0020	48	2·91	2·80
	·0040	36	2·50	2·47
	·0050	114	2·80	2·75
	·0020	32	1·03	1·01
	·0050	21	·85	·83
	·0070	38	·55	·54
Oxygen	·0030	115	2·67	2·34
	·0040	29	·72	·66
Hydrogen	·0020	25	1·83	1·66
	·0020	50	1·71	1·52
	...	18	1·39	1·38
	·0030	5	2·78	2·70
Carbon dioxide.	·0025	14	·922	·900 evoln.
	·0025	45	1·13	1·01 evoln.

view by the results obtained by Hodgson[4], who found that absorption always accompanied disintegration.

On the other hand, if chemical action were the cause of absorption, it would be reasonable to expect absorption to take place both with the normal and with the abnormal discharge.   The absence of absorption in the former case is at once explained on the disintegration–absorption theory of Soddy and Mackenzie[9].   With normal discharge there is no disintegration, and consequently the walls of the vessel do not attain the high potential reached when they are bombarded by the charged particles emitted from the cathode in the case of the abnormal discharge.   Further, when disintegration occurs, absorption is perhaps stimulated by the electrolysis of the glass of the vacuum-tube (see par. 9).
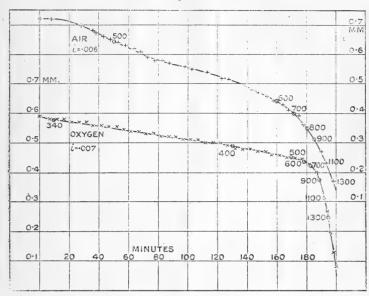
7. *Experiments with Abnormal Cathode Glow.*—In experiments with abnormal cathode glow, it was found that the rate of absorption varied with the cathode-fall, which was measured by using a fine point kept always just in the negative glow.   In air and oxygen the rate increased as the

[4] See par. 1, note 4.   [9] See par. 1, note 9.

cathode-fall increased, as is shown in fig. 3. The numbers on the curves give the cathode-fall in volts. The curves are typical of air and oxygen with copper electrodes. They can be divided into two parts, one with a small absorption rate,

Fig. 3.

and the other with a greatly increased and accelerated rate when the cathode-fall has reached a certain value. Exactly similar results were obtained in fourteen experiments in air, and five in oxygen.

The explanation of the general form of these curves is not far to seek. It is to be found in the formula given by Stark connecting the cathode-fall with the pressure [13]. Stark's formula can be written

$$V = k(C - lp)^{\frac{1}{2}}/p, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

C being the current strength, p the pressure, and V the difference between the actual cathode-fall in the abnormal state and the normal cathode-fall, which latter is constant; k and l are constants depending upon the circumstances of the experiment and the dimensions of the tube. The temperature was tolerably constant in the experiments here discussed, as the cathodes used were fairly large.

[13] Stark, *Phys. Zeit.* iii. p. 274 (1902).

We have seen that the absorption depends upon the cathode-fall being abnormal, there being no appreciable absorption when the quantity V is zero. The exact relation between V and the rate of absorption is at present but a matter for conjecture. Two possible hypotheses suggest themselves. The rate of absorption is proportional either to the excess energy of the bombarding ions, or to their excess momentum, *i. e.* either to V or to $V^{\frac{1}{2}}$. The former alternative gives

$$V \propto dp/dt, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the latter gives

$$V \propto (dp/dt)^2. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We can work out the pressure-time curve on the basis of either of these hypotheses, the current strength being assumed constant, as was the case in all the experiments here described. Using the first hypothesis we put

$$V = -mk \, dp/dt, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

m being a constant. We get

$$-mp \frac{dp}{dt} = (C - lp)^{\frac{1}{2}};$$

i. e.

$$\frac{m}{l} \frac{C - lp - C}{(C - lp)^{\frac{1}{2}}} dp = dt.$$

Integrating, we get

$$\frac{m}{l} \left\{ -\frac{2}{3l}(C - lp)^{\frac{3}{2}} + \frac{2C}{l}(C - lp)^{\frac{1}{2}} \right\} = t + A,$$

where A is an arbitrary constant. Thus we get

$$t + A = \frac{4m}{3l^2} C^{\frac{3}{2}} \left(1 - \frac{lp}{C}\right)^{\frac{1}{2}} \left(1 + \frac{lp}{2C}\right) \quad . \quad . \quad (5)$$

Put

$$lp/C = x, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

then x is always less than unity, and

$$t + A = B(1 - x)^{\frac{1}{2}} \left(1 + \frac{x}{2}\right),$$

where B is some constant. Let t_0 be the time when p has become zero, *i. e.* when $x = 0$. Then

$$t_0 + A = B.$$

Hence

$$(t - t_0)/\mathrm{B} = (1-x)^{\frac{3}{2}}\left(1 + \frac{x}{2}\right) - 1. \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

Using the second hypothesis, we put

$$\mathrm{V} = mk(dp/dt)^2, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

m being once more some constant. Then we get

$$m\left(\frac{dp}{dt}\right)^2 = \frac{(\mathrm{C}-lp)^{\frac{1}{2}}}{p},$$

i. e.

$$\frac{dt}{dp} = -m^{\frac{1}{2}}p^{\frac{1}{2}}(\mathrm{C}-lp)^{-\frac{1}{4}}, \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

the negative sign being used because the quantity dp/dt is clearly negative.

Again put

$$lp/\mathrm{C} = x, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

and we deduce

$$\frac{dt}{dx} = -\frac{m^{\frac{1}{2}}\mathrm{C}^{\frac{5}{4}}}{l^{\frac{3}{2}}}x^{\frac{1}{2}}(1-x)^{-\frac{1}{4}} \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

This cannot be integrated except by first expanding in a power series in x, and then integrating each term separately. Since x is always less than unity this is permissible. We have

$$\frac{dt}{dx} = -\frac{m^{\frac{1}{2}}\mathrm{C}^{\frac{5}{4}}}{l^{\frac{3}{2}}}x^{\frac{1}{2}}\left(1 + \frac{1}{4}x + \frac{1 \cdot 5}{4 \cdot 8}x^2 + \ldots\right). \quad \cdot \quad (11)$$

Hence

$$t = \mathrm{A}' - \mathrm{B}'x^{\frac{3}{2}}\left(\frac{1}{3} + \frac{1}{4}\frac{x}{5} + \frac{1 \cdot 5}{4 \cdot 8}\frac{x^2}{7} + \ldots\right),$$

A', B' being some constants.

Again, if t_0 is the time when the whole of the gas in the tube has been absorbed, we get
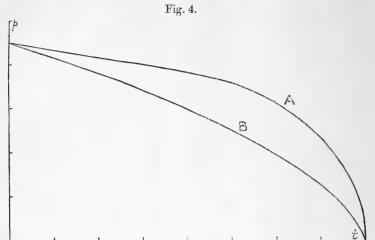
$$t_0 = \mathrm{A}',$$

and therefore

$$\frac{t - t_0}{\mathrm{B}'} = -x^{\frac{3}{2}}\left(\frac{1}{3} + \frac{1}{4}\frac{x}{5} + \frac{1 \cdot 5}{4 \cdot 8}\frac{x^2}{7} + \ldots\right) \quad \cdot \quad \cdot \quad (12)$$

The curves given by the equations (7) and (12) have been
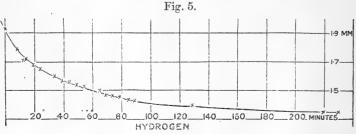
plotted in fig. 4, A and B respectively. It seems that the first hypothesis, giving the curve A in fig. 4, is the more satisfactory one. A good test would be to perform a series of experiments between the same limits of x, but with

Fig. 4.

different current strengths. The time occupied by the absorption should be proportional to the one and a half power of the current strength. Such experiments would perhaps be rather long and laborious.
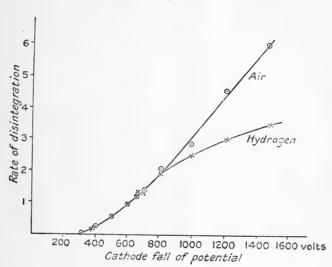
Attempts to obtain a relation between the cathode-fall and the rate of absorption from the data supplied by the results of our experiments, met with only partial success. The mathematical investigation suggests the relation to be one of proportionality, but there is no doubt that the cathode-fall as recorded was subject to considerable experimental error due to lag, especially for small and for very large values of V.

Fig. 5.

HYDROGEN

In the case of hydrogen, quite a different type of curve was obtained, fig. 5. The absorption was at first rapid, and

then diminished to zero. At first sight, this would seem to be in direct opposition to the disintegration theory, but an examination of Tyndall and Hughes' curves shows that the case of hydrogen lends additional support to this theory. Fig. 6 is reproduced from their paper. In air, the gradient

Fig. 6.

Cathode fall of potential

in the rate of disintegration increases as the cathode-fall increases; the rate of absorption also increases under the same conditions. In hydrogen, the gradient in the rate of disintegration soon decreases with increase of cathode-fall, tending towards zero; the rate of absorption also decreases with increasing cathode-fall, tending towards zero. The exact parallelism between the rates of absorption and the gradients in the rate of disintegration in these widely divergent results is an excellent verification of the theory advocated in this paper.

8. *General Discussion.*—The absorption is probably a phenomenon of some complexity. With metallic electrodes, the major portion is due to absorption of gas by the disintegrated metal. Some may be due to the liberation of the alkali metals by electrolysis of the glass, and chemical combination of these metals with the gas. Experiments in tubes made of other materials than glass would be of great

interest in this connexion. Many of the apparently contradictory results obtained by different experimenters can be reconciled by means of the dual explanation here suggested.

Willows[1] concluded that the absorption was chemical in origin, because he found its rate to vary according to the particular nature of the glass from which the tube was made. The absorption was biggest in soda glass, less in lead glass, and least in Jena glass. If the glass is electrolysed this is exactly what one would expect. During the passage of a discharge the glass becomes highly charged, as was shown by Riecke[14], and may easily be electrolysed, especially if heated by the cathode rays. Warburg, in fact, used this to obtain a film of metallic sodium on the inside of vacuum-tubes for the purpose of purifying gases[15]. Mey's[2] results show that when sodium and potassium amalgams are used as electrodes, compounds of these metals with hydrogen and nitrogen can be formed, suggesting that the same compounds can be formed with the alkali metals in the glass. The fact that Hill obtained an absorption with the electrodeless discharge[6] can similarly be explained on the hypothesis that the glass is electrolysed, the metal liberated causing the absorption observed.

Hill found that if successive absorption experiments are performed, the absorption gradually decreases. This is again in agreement with the theory that part of the absorption is due to the electrolysis of the glass, for as the soda glass used by him became more and more electrolysed, the sodium was gradually used up, and the absorption naturally diminished.

It was also found by Hill that an experiment in oxygen followed up by one in hydrogen gave an accelerated rate of absorption in the latter. He offers as an explanation of this fact the suggestion that the cause of absorption in the oxygen experiment was oxidation, and then if we use hydrogen immediately afterwards, there is a reduction, and consequently a rapid absorption. This may be the case. But in fig. 6 the authors show the typical absorption curve for hydrogen, there being a rapid absorption at once, whether a previous experiment has been performed in oxygen

[1] See par. 1, note 1.
[14] Wied. *Ann.* iii. p. 414 (1899).
[15] *Ann. d. Phys.* xl. p. 2 (1890).
[2] See par. 1, note 2.
[6] See par. 1, note 6.

or not. Curves V., VIII., IX., X., in Hodgson's paper[4], show the rapid absorption in hydrogen after the tube has rested awhile, an initial rapid absorption being obvious in each case. It appears, therefore, that the initial rapid absorption is due solely to the hydrogen, and does not depend upon the tube having been used with oxygen immediately preceding the hydrogen experiment.

Further, the fact that the inactive gases helium and argon are readily absorbed, shows that means other than chemical must be at work.

In 1907 Campbell Swinton found that gas was occluded in the walls of the glass vacuum-tubes after discharge[7]. This gas was found in the form of bubbles a little below the surface of the glass. But in 1908 Soddy and Mackenzie obtained the Campbell Swinton effect[9], and found that the gas occurring as bubbles was probably due to the electrolysis of undecomposed carbonates and sulphates in the glass. The gas absorbed by the discharge was found by them to be not in the glass but in the film deposited from the cathode by disintegration, and a large fraction of the absorbed gas could be recovered. They also showed that sublimated magnesium or aluminium did not absorb helium. It was, however, shown by Heald[16] that many metals absorb hydrogen on sublimation in a vacuum-tube. Heald worked with hydrogen and his curves are typical absorption curves for hydrogen. The absorption in a vacuum-tube is thus not a mechanical occlusion, but is brought about by some electrical means.

Skinner[17] concluded that gas was evolved from the cathode and absorbed by the anode. With new electrodes there is often an initial evolution of gas especially in hydrogen and nitrogen, or in any gas with aluminium electrodes. But if the tube is used and then allowed to stand awhile, on restoring the current, no initial evolution is found in most cases. The evolution that Skinner speaks of must refer to fresh or virgin electrodes, and is probably due to the state of the surface with regard to its gas content.

In the case of aluminium, gas is evolved for a long time before absorption sets in. In Hodgson's curves XXXV., XXXVI.[4], the pressure curves for copper anode–aluminium

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[4] See par. 1, note 4.   [7] See par. 1, note 7.   [9] See par. 1, note 9.
[16] Phys. Rev. xxiv. p. 269 (1907).
[17] Phil. Mag. xii. p. 481 (1906) ; Phys. Rev. xxi. pp. 1 & 169 (1905) ; *Phys. Zeit.* vi. p. 610 (1905).
[4] See par. 1, note 4.

cathode, and for copper cathode–aluminium anode are shown. In the former case gas was evolved for a long period, and absorption did not set in at all. In the latter, absorption occurred after the passage of a few coulombs. The probable explanation is that disintegration did not set in at all in the first case, and hence there was no absorption, whereas in the latter case disintegration, and therefore also absorption, set in early in the experiment.

Riecke[8] concluded from some of his experiments that a fraction of the atoms bombarding the cathode are absorbed. He was unaware of the changes in the rate of absorption that occur after a tube is rested, and neglected them. That they are considerable is apparent from curves VIII., IX., XXXV., and others in Hodgson's paper[4].

The apparatus used in the above experiments was obtained by a grant from the Research Fund of the University of Bristol Colston Society.

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LVI. *Note on the Expansion of a Function.* By I. J. Schwatt [*].

TO expand

$$(\tan^{-1} x)^p, \qquad -\frac{\pi}{4} < x < \frac{\pi}{4},$$

in powers of x.

$$\tan^{-1} x = \int_0^x \frac{dx}{1+x^2} = \sum_{\kappa=1}^{\infty} (-1)^{\kappa-1} \frac{x^{2\kappa-1}}{2\kappa-1} \quad \cdots \quad (1)$$

and

$$(\tan^{-1} x)^2 = 2 \int_0^x \frac{\tan^{-1} x}{1+x^2} dx$$

$$= 2 \int_0^x \sum_{\kappa=1}^{\infty} (-1)^{\kappa-1} \frac{x^{2\kappa-1}}{2\kappa-1} \sum_{a=1}^{\infty} (-1)^{a-1} x^{2a-2} dx.$$

[8] See par. 1, note 8.   [4] See par. 1, note 4.
[*] Communicated by the Author.

Letting $\kappa + \alpha = \beta$, we have

$$\sum_{\kappa=1}^{\infty} (-1)^{\kappa-1} \frac{x^{2\kappa-1}}{2\kappa-1} \sum_{\alpha=1}^{\infty} (-1)^{\alpha-1} x^{2\alpha-2} = \sum_{\kappa=1}^{\infty} \sum_{\beta=\kappa+1}^{\infty} (-1)^{\beta} \frac{1}{2\kappa-1} x^{2\beta-3},$$

$$= \sum_{\beta=2}^{\infty} (-1)^{\beta} x^{2\beta-3} \sum_{\kappa=1}^{\beta-1} \frac{1}{2\kappa-1},$$

$$= \sum_{\beta=1}^{\infty} (-1)^{\beta+1} x^{2\beta-1} \sum_{\kappa=1}^{\beta} \frac{1}{2\kappa-1}$$

Therefore

$$(\tan^{-1}x)^2 = 2 ! \sum_{\kappa=1}^{\infty} (-1)^{\kappa-1} \frac{x^{2\kappa}}{2\kappa} \sum_{\kappa_1=1}^{\kappa} \frac{1}{2\kappa_1-1} \cdot \quad \cdots \quad (2)$$

Again

$$(\tan^{-1}x)^3 = 3 \int_0^x \frac{(\tan^{-1}x)^2}{1+x^2} dx$$

$$= 3 \cdot 2 ! \int_0^x \sum_{\kappa=1}^{\infty} (-1)^{\kappa-1} \frac{x^{2\kappa}}{2\kappa} \sum_{\kappa_1=1}^{\kappa} \frac{1}{2\kappa_1-1} \sum_{\alpha=1}^{\infty} (-1)^{\alpha-1} x^{2\alpha-2} dx,$$

$$= 3 ! \int_0^x \sum_{\kappa=1}^{\infty} \frac{1}{2\kappa} \sum_{\kappa_1=1}^{\kappa} \frac{1}{2\kappa_1-1} \sum_{\beta=\kappa+1}^{\infty} (-1)^{\beta} x^{2\beta-2} dx,$$

$$= 3 ! \int_0^x \sum_{\beta=2}^{\infty} (-1)^{\beta} x^{2\beta-2} \sum_{\kappa=1}^{\beta-1} \frac{1}{2\kappa} \sum_{\kappa_1=1}^{\kappa} \frac{1}{2\kappa_1-1} dx.$$

Hence

$$(\tan^{-1}x)^3 = 3 ! \sum_{\kappa=1}^{\infty} (-1)^{\kappa-1} \frac{x^{2\kappa+1}}{2\kappa+1} \sum_{\kappa_1=1}^{\kappa} \frac{1}{2\kappa_1} \sum_{\kappa_2=1}^{\kappa_1} \frac{1}{2\kappa_2-1} \cdot \quad \cdots \quad (3)$$

We now assume that

$$(\tan^{-1}x)^p = p ! \sum_{\kappa_0=1}^{\infty} (-1)^{\kappa_0-1} \frac{x^{2\kappa_0+p-2}}{2\kappa_0+p-2} \prod_{a=1}^{p-1} \left(\sum_{\kappa_a=1}^{\kappa_{a-1}} \frac{1}{2\kappa_a + p - a - 2} \right), \quad (4)$$

then

$$(\tan^{-1}x)^{p+1} = p!(p+1) \int_0^x \frac{(\tan^{-1}x)^p}{1+x^2} dx,$$

$$= (p+1) ! \int_0^x \sum_{\kappa_0=1}^{\infty} (-1)^{\kappa_0-1} \frac{x^{2\kappa_0+p-2}}{2\kappa_0+p-2} \prod_{a=1}^{p-1} \left(\sum_{\kappa_a=1}^{\kappa_{a-1}} \frac{1}{2\kappa_a + p - a - 2} \right)$$

$$\times \sum_{\gamma=1}^{\infty} (-1)^{\gamma-1} x^{2\gamma-2} dx,$$

$$= (p+1)\,!\int_0^x \sum_{\kappa_0=1}^\infty \frac{1}{2\kappa_0+p-2}\prod_{a=1}^{p-1}\left(\sum_{\kappa_a=1}^{\kappa_{a-1}}\frac{1}{2\kappa_a+p-a-2}\right)$$

$$\times \sum_{m=\kappa_0+1}^\infty (-1)^m x^{2m+p-4}dx,$$

$$= (p+1)\,!\int_0^x \sum_{m=2}^\infty (-1)^m x^{2m+p-4}\left(\sum_{\kappa_0=1}^{m-1}\frac{1}{2\kappa_0+p-2}\right)$$

$$\times \prod_{a=1}^{p-1}\left(\sum_{\kappa_a=1}^{\kappa_a-1}\frac{1}{2\kappa_a+p-a-2}\right)dx,$$

$$= (p+1)\,!\sum_{m=1}^\infty (-1)^{m-1}\frac{x^{2m+p-1}}{2m+p-1}\left(\sum_{\kappa_0=1}^{m}\frac{1}{2\kappa_0+p-2}\right)$$

$$\times \prod_{a=1}^{p-1}\left(\sum_{\kappa_a=1}^{\kappa_a-1}\frac{1}{2\kappa_a+p-a-2}\right).$$

Replacing m by κ_0 and κ_{a-1} by κ_a we obtain

$$(\tan^{-1}v)^{p+1}=(p+1)\,!\sum_{\kappa_0=1}^\infty (-1)^{\kappa_0-1}\frac{v^{2\kappa_0+p+1-2}}{2\kappa_0+p+1-2}\sum_{\kappa_1=1}^{\kappa_0}\frac{1}{2\kappa_1+p+1-1}$$

$$\times \prod_{a=2}^{p+1-1}\left(\sum_{\kappa_a=1}^{\kappa_a-1}\frac{1}{2\kappa_a+p+1-a-2}\right),$$

$$= (p+1)\,!\sum_{\kappa_0=1}^\infty (-1)^{\kappa_0-1}\frac{v^{2\kappa_0+p+1-2}}{2\kappa_0+p+1-2}$$

$$\times \prod_{a=1}^{p+1-1}\left(\sum_{\kappa_a=1}^{\kappa_a-1}\frac{1}{2\kappa_a+p+1-a-2}\right), \quad . \quad . \quad (5)$$

which is of the same form as the expression (4), p being replaced by $p+1$. Hence reasoning by induction (4) is true for all positive values of p.

Therefore assuming $\prod_{a=1}^{0} A_a=1$, we have

$$(\tan^{-1}v)^p=p\,!\sum_{\kappa_0=1}^\infty (-1)^{\kappa_0-1}\frac{v^{2\kappa_0+p-2}}{2\kappa_0+p-2}\prod_{a=1}^{p-1}\left(\sum_{\kappa_a=1}^{\kappa_a-1}\frac{1}{2\kappa_a+p-a-2}\right).$$

Thus

$$\tan^{-1}x = 1 \, ! \left[x - \frac{x^3}{3} + \frac{x^5}{5} - \frac{x^7}{7} + \ldots \right]$$

$$(\tan^{-1}x)^2 = 2 \, ! \left[\frac{x^2}{2} - \left(1 + \frac{1}{3} \right) \frac{x^4}{4} + \left(1 + \frac{1}{3} + \frac{1}{5} \right) \frac{x^6}{6} \right.$$
$$\left. - \left(1 + \frac{1}{3} + \frac{1}{5} + \frac{1}{7} \right) \frac{x^8}{8} + \ldots \right],$$

$$(\tan^{-1}x)^3 = 3 \, ! \left[\frac{1}{2} \frac{x^3}{3} - \left\{ \frac{1}{2} + \frac{1}{4} \left(1 + \frac{1}{3} \right) \right\} \frac{x^5}{5} + \left\{ \frac{1}{2} + \frac{1}{4} \left(1 + \frac{1}{3} \right) \right. \right.$$
$$\left. \left. + \frac{1}{6} \left(1 + \frac{1}{3} + \frac{1}{5} \right) \right\} \frac{x^7}{7} - \ldots \right],$$

etc.

University of Pennsylvania,
Philadelphia, Pa., U.S.A.

LVII. *Notices respecting New Books.*

Tables for Statisticians and Biometricians. Edited by
Prof. KARL PEARSON. 9s. (Cambridge University Press.)

THIS volume contains 55 tables and abacs, with an introduction
of some 83 pages giving particulars of their use. The tables
fall into three groups. The first group centres round the pro-
bability integral. If N is the total number of observations, m the
mean value, and z the frequency of an observation of magnitude x,
then

$$z = \frac{N}{\sqrt{2\pi}\sigma} \exp - (x-m)^2/2\sigma^2,$$

where σ is a constant characteristic of the distribution. Four
tables enable the reader to find any two of z, $\frac{x}{\sigma}$, $\int_x^\infty z\,dx - \int_{-\infty}^x z\,dx$,
i. e. the ordinate, the abscissa, and the difference of the areas of the
two parts into which the ordinate divides the probability curve, when
the third is given. Other tables give $\int_0^x x^n e^{-\frac{x^2}{2}}\,dx$, and enable
the whole curve to be reconstructed from data concerning a portion
of it.

The table for testing goodness of fit is founded on the above
normal law of error, and may be considered to belong to this group.
It deserves to be better known. Let $f_1', f_2', f_3', \ldots f_n'$ be observed
frequencies corresponding to $x_1, x_2, x_3, \ldots x_n$. Let $z = \varphi(x)$ be a

theoretical frequency distribution meant to describe the above, giving theoretical values $f_1 = \phi(x_1)$, $f_2 = \phi(x_2)$ .... Then if $\chi^2 = \Sigma \left(\dfrac{f-f'}{f}\right)^n$ be calculated, P corresponding to this χ^2 is found from Table XII, and gives the probability that in a repeated set of observations the actual frequencies will differ from the theoretical ones (this difference being measured by χ^2) as much or more. If this probability is high, the fit is good.

The second group is intended to simplify the calculation of the constants in the group of frequency curves introduced by Prof. Pearson as generalizations of Gauss's normal curve. Gauss assumed (i.) the equal probability of errors in excess of the mean and errors in defect, (ii.) the continuity of magnitude in the errors, and (iii.) the independence of all the small contributions to the total error. This leads to $\dfrac{1}{y} \cdot \dfrac{dy}{dx} = -\dfrac{x}{\sigma^2}$, or $y = c e^{-\frac{x^2}{2\sigma^2}}$. Prof. Pearson drops these assumptions and finds

$$\frac{1}{y} \cdot \frac{dy}{dx} = \frac{x+d}{a+bx+cx^2},$$

leading to curves of seven types (five more have since been discovered) of which Gauss's is one, and

$$y = c \left(1 - \frac{x}{a}\right)^{ma} \left(1 + \frac{x}{b}\right)^{mb} \quad \text{is another.}$$

Tables XXVI–XXXI. and XLIX. include a table of Gamma functions, logarithms of factorials, the powers and sums of powers of natural numbers. The latter are especially useful for solving numerical algebraical equations of high degree.

The third group deals with correlations and with probable errors of the constants employed. Briefly, if

$$z = A \exp -\frac{(x-m_1)^2}{2\sigma_1^{\,2}} - \frac{(y-m_2)^2}{2\sigma_2^{\,2}}$$

gives the frequency distribution of deviations of x and y from their means, then these deviations are independent; but if

$$z = A \exp -\frac{(x-m_1)^2}{2\sigma_1^{\,2}} - \frac{(y-m_2)^2}{2\sigma_2^{\,2}} - \frac{2(x-m_1)(y-m_2)}{2\sigma_1\sigma_2},$$

the deviations are no longer independent: r is the coefficient of correlation ranging in value from -1 to $+1$ and measures the dependence, and most of the tables in this section are intended to give the value of r and the degree of its accuracy with a minimum of labour from a minimum of data. Particular attention is devoted to the determination of r from a fourfold table, as this case frequently occurs in the current work of medical statistics

and experimental psychology, and requires the solution of a complicated transcendental equation. The tables obviate this.

The Tables will be of great value to psychologists and others who use modern statistical formulæ, and have not had the opportunity to acquire the mathematics that will enable them to estimate the significance of their results, as the tables enable the probable errors (which mean troublesome mathematics) to be read off.

Considering the great amount of labour in calculating the tables and the expense in printing and publishing them, the price of the book is very reasonable. It is hoped that Prof. Pearson will be able in the near future to fulfil his promise to issue a second and larger edition of this work.

LVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 416.]

June 23rd, 1915.—Dr. A. Smith Woodward, F.R.S., President, in the Chair.

THE following communications were read :—

1. ' On a New Eurypterid from the Belgian Coal Measures.' By Prof. Xavier Stainier.

2. ' On a Fossiliferous Limestone from the North Sea.' By Richard Bullen Newton, F.G.S.

3. ' The Origin of the Tin-Ore Deposits of the Kinta District, Perak (Federated Malay States).' By William Richard Jones, B.Sc., F.G.S.

Certain tin-ore-bearing clays and boulder-clays occurring in the Kinta district have been described by Mr. J. B. Scrivenor, Government Geologist, F.M.S., as being of glacial origin, and the tin-ore which they contain as having been derived from ' some mass of tin-bearing granite and rocks altered by it, distinct from and older than the Mesozoic Granite ' (that is, than the granite now *in situ* in the Kinta district). These stanniferous clays and boulder-clays are stated to have furnished a more valuable horizon on climatic evidence than can be afforded by limited collections of fossils in rocks far removed from Europe, and have been correlated with the Talchirs of India and mapped as Older Gondwana rocks.

It would be difficult to overestimate the importance of the origin of these clays in a country where, on the one hand, they yield a very important part of the world's output of tin-ore, and where, on the other, they have been used as the horizon on which to base the geological age of rocks which cover about a third of the surface of the Malay Peninsula. If of glacial origin, a vast tin-field remains to be discovered.

The object of this paper is to show that all the tin-ore found in these clays is derived from rocks now *in situ* in the Kinta district; that it is not necessary to bring in glacial action to explain any of the features which led to the adoption of the theory of their glacial origin; to point out that these deposits cannot be correlated with the Talchirs of India; and to show that a simple interpretation may be given to the geology of the Kinta district.

The sources of the tin-ore here are: (1) the stanniferous granite of the Main Range and of the Kledang Range; (2) other granite outcrops known to carry cassiterite; (3) the granitic intrusions in the phyllites and schists, notably near the granite-junction; and (4) the granitic intrusions traversing the limestone, and forming an important source of ore.

The angularity of the boulders and of the tin-ore in some of these clays is due (1) to weathering *in situ* of the phyllites and schists, which then sink on the dissolving limestone underneath; (2) to soil-creep effecting the same result; (3) to the breaking-up of the much-weathered cassiterite-bearing boulders and pebbles in the alluvium.

Over 90 per cent. of the ore worked in the whole of the Kinta district is obtained from mines situated at less than a mile from granite or from granitic intrusions.

LIX. *Intelligence and Miscellaneous Articles.*

ON MUTUAL- AND SELF-INDUCTANCE SERIES.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN my paper on "Mutual- and Self-Inductance Series" which appeared in the Philosophical Magazine for April, I stated that the formulæ for the mutual induction between coaxial circles had only been completely determined in the case of circles far apart. Since the publication of the paper my attention has been drawn to two papers published by Dr. T. J. I'a. Bromwich (Quarterly Journal of Pure and Applied Mathematics, No. 176, pp. 363, 381, 1913), in which a number of the formulæ given by me for circles close together are obtained by a method which is substantially the same as the one I used.

I wish to take this opportunity of apologizing to Dr. Bromwich for trespassing on ground already covered by him, and to assure him that I was totally unacquainted with his work in this direction until a few days ago.

<div style="text-align:right">

Yours faithfully,
S. BUTTERWORTH.

</div>
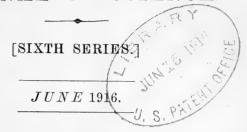
School of Technology,
    Manchester.
        April 7th, 1916.

LX. *The Variation of the Positive Emission Currents from Hot Platinum with the Applied Potential Difference.* By O. W. Richardson, *F.R.S., Wheatstone Professor of Physics, University of London, King's College,* and Charles Sheard, *Professor of Applied Optics, Ohio State University* *.

THE incentive to the present investigation was an observation recorded by one of the authors † to the effect that when a fresh metal wire is positively charged and heated in a vacuum, the relation between current and electromotive force, when due allowance is made for the decay of the current with time, is approximately linear, although it is known that no measurable quantity of negative ions is emitted by the wire at the temperature of the experiment. Since one would expect saturation to occur with a quite small potential under these circumstances, this phenomenon seemed to call for further examination.

The experiments have been made with two forms of testing vessel:—(1) A glass tube in which the electrodes are a loop of heated platinum wire and a platinum plate. This tube is identical with the one figured in Phil. Trans. A. vol. ccvii. p. 4, fig. 1 (1906). (2) A brass cylinder with an axial platinum wire. The wires were heated electrically, the temperature being controlled and measured by placing the wires in one arm of a Wheatstone's bridge, which was

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* Communicated by the Authors.
† O. W. Richardson, Phil. Mag. vol. vi. p. 80 (1903).
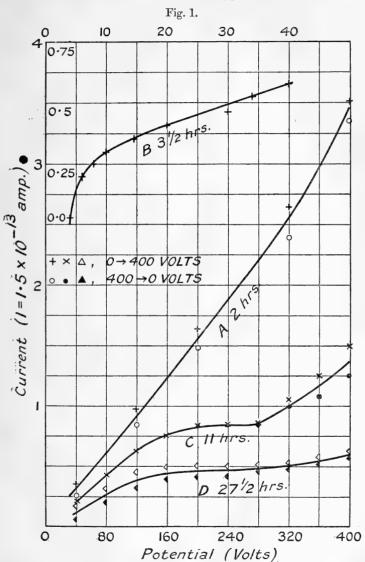
actuated by the main heating-current in the usual way. The potentials were applied at the mid-point of a high resistance which shunted the wire outside the tube : they therefore represent the average potential of the hot wire. We aimed to work at as low temperature and with as small currents as possible so as to eliminate the time-decay of the positive emission. The currents were measured with a delicate electrometer. The platinum wire in the glass tube was Johnson & Matthey's purest resistance wire ; that used in the other experiments was ordinary commercial platinum and had a very low temperature coefficient of resistance (·00165 per ° C.). The pressure recorded on the McLeod gauge was between the limits 0·00005 and 0·0002 in all the experiments.

In the first observations with the glass tube and platinum plate-electrode the temperature was adjusted to 451·5 ± 1°·5 C. Successive curves showing the relation between the current and applied voltage at different times are exhibited in fig. 1. The first current-E.M.F. curve was not completed until about $2\frac{1}{2}$ hours had elapsed from the commencement of the heating, as some time was occupied in preliminary adjustments. It is marked A in the figure. The curve is slightly convex to the voltage axis, but is almost linear, in agreement with the one referred to above published by one of the writers. The approximately linear relation did not hold down to V = 0, but the curves became concave to the voltage axis at low voltages as shown in curve B, which is on a different scale. All the potentials in fig. 1 are about 4 volts too high on account of the measured potential not being that at the middle of the hot wire.

As the heating of the wire was continued the first effect was to rotate the curve A about O towards the potential axis. This corresponds to a decay of the currents in approximately equal proportions at all potentials. With further heating the curves developed a flat region in the middle, as is shown by curve C, which was obtained after 11 hours heating. With subsequent heating the increased current above 280 volts continues to decrease faster than the currents at lower voltages, until after about 30 hours it is scarcely noticeable. The result of heating for $27\frac{1}{2}$ hours is shown in curve D. The observations both with rising and with falling potentials are shown in the figure. The difference between them is not very great in most instances, but when there is an appreciable difference the currents with rising potentials, which were measured first, are larger (see below). It is important to remember that in these experiments the temperatures were so low that several hours were necessary for the emission to

decay a few per cent. After the stage showing saturation between 100 and 400 volts had appeared, this form of

Fig. 1.
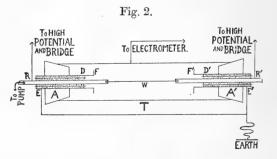
current-E.M.F. curve apparently persisted indefinitely. The only change observed subsequently, on heating at constant temperature, consisted in a uniform decay of the total current at all voltages.

2 L 2

Before these experiments were made, the tube, which contained nothing but glass and platinum, was carefully boiled out with pure nitric acid and distilled water. The tube was dried in a current of warm air before connecting to the Gaede pump and pentoxide bulb. It was exhausted at a pressure of less than 0·0001 mm. on the McLeod gauge before the wire was heated. The diameter of the wire was 0·15 mm. and its length 5 cm.
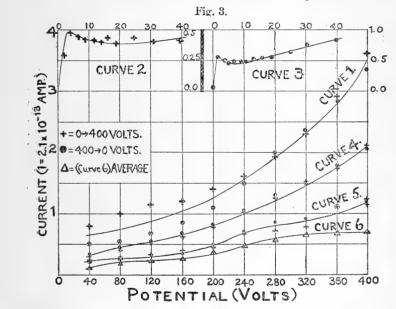
The results described above were obtained when the wire was continuously maintained at the temperature at which the emission was measured. After heating the wire, which was positively charged, to a relatively high temperature (718° C.), and subsequently observing at the original temperature (452° C.), the resulting current-E.M.F. curves were very peculiar. They were characterized by a very sharp maximum at about 240 volts, which was more marked with descending than with rising potentials. It seemed to us that these peculiarities might be due to the glass insulation becoming charged to a high potential under the influence of the copious emission of positive ions which had occurred at the higher temperature. The brass-tube apparatus shown in fig. 2 was therefore constructed in order to eliminate this possibility.

Fig. 2.

The platinum wire W was stretched along the axis of the brass tube T which, suitably supported and properly shielded, formed the receiving electrode. The wire W was welded to two stout platinum end-pieces, which in turn were soldered respectively to the brass rod R′ and the tube R. This was done to prevent the solder from coming into contact with the hot part of the platinum and causing it to rot. R and R′ were supported by glass tubes surrounded by earthed brass tubes, E and E′, provided with flanges, F and F′. E and E′ were supported by rubber stoppers, A and A′. The only insulation in this arrangement which the ions

could have access to consists of the rubber stoppers A and A', and the glass tubes, and all of this is shielded from the ions by metal screens. There is thus no possibility of trouble from the insulation charging up. The joints were cemented with sealing-wax and soft wax. There was no difficulty in maintaining a vacuum of 0·0002 mm. or less, as indicated by the McLeod gauge reading.

Broadly speaking, the time-changes with the new apparatus were similar to those observed with the glass tube. A selection from a series of observations is exhibited in fig. 3. The temperature in the different experiments was

Fig. 3.

equal to $379 \pm 1°$ C. The time which elapsed, after the heating commenced, up to the beginning of each curve was approximately as follows :—Curve 1, 0 ; curve 2, $1\frac{1}{2}$ hours ; curve 3, 2 hours ; curve 4, 7 hours ; curve 5, 30 hours ; curve 6, 48 hours. The initial curves are more curved to the current axis than those observed with the glass tube under similar conditions. In curve 1 the points shown thus + were taken with rising, those shown thus ● with falling potentials. When the potential is raised the current is exceptionally large at first and *vice versa*. The final approximately steady values of the current would lie about half way between the sets of points, as is shown by the curve. The current-E.M.F. curves for low potentials
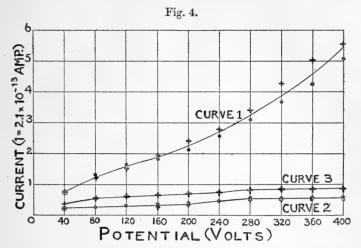
(Nos. 2 and 3) are peculiar, although similar observations have been recorded before by one of the writers [*]. The current is greater in the neighbourhood of 2–4 volts than it is at somewhat higher potentials, indicating that one of the effects of increasing the applied potential is to diminish the number of systems giving rise to the emission. Curves showing this maximum current at a low potential were obtained after the wire had been heated at 379° C. for 50 hours, and then at a temperature of 600° C. for 2 hours just before the observations were made. On the other hand, some curves taken at intermediate intervals showed a continuous increase of current with increasing potential difference. This shows that the maximum is not determined solely by some peculiarity in the initial condition of the wire. We have not discovered what the determining factor is.

Fig. 3 shows that the proportional rate of decay of the current at 400 volts is greater than that at moderate potentials, for example, 200 volts, although this effect is much less marked than in fig. 1. Thus, comparing curves 1 and 6, the ratio of the ordinates at 400 volts is about 5 to 1, whereas at 280 volts it is only a little over 3 to 1. After continued heating the results show a tendency to become more irregular, but the main features exhibited in curve 6 were obtained too frequently to be likely to be due to observational errors. These features are (1) a steady rise to a flat region between 80 and 160 volts, (2) a further rise from 160 to 280 volts, followed by (3) a comparatively flat region between 320 and 400 volts. This type of curve seems to point to the existence either of two different types of ions or of two different processes involved in the emission. These particular indications of duplicity were not noticeable in the first apparatus. A later stage obtained after further heating is shown in fig. 4, curve 2.

We shall now consider a number of ways in which a tube giving curves like those shown in fig. 3, curve 6, may be made to exhibit curves like fig. 3, curve 1, again. This is found to happen if air at atmospheric pressure is admitted into the tube, and then pumped out again before the observations are taken, and also if the wire is heated for a time at a somewhat higher temperature than that at which the previous and subsequent tests are carried out. The general nature of these effects is the same in all cases, so that it will be sufficient to consider one instance in detail. The wire in the brass tube after continued heating gave the curve marked

[*] O. W. Richardson, Phil. Trans. A. vol. ccvii. pp. 10–11 (1906).

curve 2 in fig. 4 at 344° C. The heating current was then cut off, and air at atmospheric pressure allowed to remain in the tube for 22 hours. It was then pumped out to a pressure of 0·0002 mm. on the McLeod gauge and the wire again heated

Fig. 4.

at 342° C. It then gave curve 1, fig. 4. Our experiments show that this freshening action produced by admitting air diminished with successive repetitions of the process, but we did not succeed in reaching a stage at which the air ceased to produce an effect. The effect occurred both when the inner surface of the brass tube was left untouched and when it was thoroughly scraped with emery-paper. The increased sensitiveness could not be removed by mere pumping. In one case, the tube, after exposure to air, was pumped out for 15 hours at a pressure below 0·0002 mm. and still found to give a curve practically identical with fig. 4, curve 1.

Similar effects were observed when the wire was raised for a time to a higher temperature than that at which the observations of the positive current were made. Thus, after taking curve 6, fig. 3, the hot wire, under zero potential, was kept at 600° C. for 2 hours. The temperature was then reduced to the previous value (378° C.) and another curve taken. The new curve was found to be similar to curve 1 of fig. 3. The current at 400 volts had been increased in the ratio of about 4 to 1 by this treatment. Results of the same character were obtained with the glass-tube apparatus.

The changes were more pronounced when the hot wire was negatively charged and discharging electrons to the cold electrode during the temporary heating. In a particular

instance, the current, after continued heating with the wire
positively charged at 342° C., gave an almost constant current
which only increased from 0·6 div. per sec. at +120 volts
to 0·75 div. per sec. at +400 volts. The wire was then
heated for 30 minutes at 595° C. and −400 volts. The
negative emission was measurable at this temperature. On
returning to 342° C. and +400 volts, the initial current was
found to be equal to 14 divisions per sec., or about 20 times
the previous value. This large current fell away fairly
rapidly with time at the lower temperature (342° C.), as is
shown in the following numbers :—

Current in divs. per sec.	14	10	8	5·1	3·4	2·6	1·8	1·25	1·05	1·00
Time in minutes	0	5	10	25	35	45	60	75	85	100

The negative currents which were used to stimulate the
tube in these experiments were quite small. They varied
a little, but always of the order of 10^{-13} amp. The
relation between current and potential for the positive leak
in the stimulated tube appeared to depend a good deal on its
previous history. The curves obtained at first showed an
almost linear relation between current and potential from
40 to 400 volts, after allowing for the time factor. With
successive stimulations the curves became more concave to
the potential axis, until finally they were almost saturated
all the way from +40 to +400 volts. It appears therefore
that, with successive treatments, the tube gets into such a
state that the passage of a negative discharge from the wire
at a higher temperature produces an increase in the posi-
tive emission, subsequently measured at the original lower
temperature, which does not increase with the applied
potential at high potentials. This increase is still of the
order of magnitude, even at +400 volts, of that which is
observed in the earlier stages and dies away with time at a
rate which is of the same order of magnitude.

The progressive increase of the currents, with increasing
potential difference, which has been recorded in the various
cases tested, might be due to a variety of causes. Recom-
bination, which is the most important factor preventing the
attainment of saturation in the usual cases of ionization of
gases at moderate pressures, does not occur here, as there is
no current, at the temperatures at which the positive emis-
sion was measured, when the wire is charged negatively.
Ionization of the surrounding gas by collisions would not be
expected to be a serious factor on account of the smallness
of the pressures. We are thus limited either to an effect of

the electric field on the emission at the hot wire, or to an effect which it may produce indirectly by the impact of the ions on the negative electrode. Some experiments which we made led us to conclude that the second of these alternatives was the correct one [*]. In these experiments it appeared that the large currents at high potentials could be cut down by the application of rather small transverse magnetic fields, indicating that the carriers of part of the discharge were negative electrons liberated at the cold electrode. However, further experiments showed that this influence of a magnetic field was not always to be relied on ; so that the results of this test cannot be regarded as decisive. At this stage we were compelled to discontinue the experiments, which were made in the Palmer Laboratory at Princeton University. At the suggestion of one of us the further investigation of these phenomena was undertaken by Mr. H. H. Lester, whose results will shortly be published in this journal.

LXI. *The Infra-red and Ultra-violet Absorption of Sulphur Dioxide and their Relation to the Infra-red Spectra of Oxygen and Hydrogen Sulphide. By* C. Scott Garrett, *B.Sc.*[†]

IN a recent paper on the absorption of sulphites and sulphur dioxide, the equilibrium conditions existing in the aqueous solutions of these substances were investigated, and it was intimated that further data on the absorption of sulphur dioxide would be published separately [‡]. The present paper deals with these data and contains a detailed study of the gaseous absorption of sulphur dioxide, which was undertaken more especially to test the applicability of Baly's theory of the connexion between ultra-violet and infra-red absorption [§]. This theory, which is based on the energy quantum theory and Bjerrum's work, has found considerable experimental support in the absorption spectra of benzene and certain other organic compounds, and it was thought probable that it could be put to a more extended test by an investigation of the absorption system of sulphur

dioxide. The apparatus employed consisted of a quartz-ended glass cell of special construction connected by glass tubing to a reservoir containing the dry gas and to a mercury manometer. As the light source, the condensed spark between nickel electrodes was used and the absorptive power was determined by photography with the help of a quartz spectrograph and a Hilger rotating sector photometer.

As is well known, the broad absorption band exhibited by sulphur dioxide in the liquid and solution phases is resolved into a number of small band groups which, at any rate in the less refrangible ultra-violet region, are symmetrically distributed around a central band group of maximum absorption. By varying the pressure and the thickness of the absorption layer of the gas, the temperature being kept constant, I have been able to trace out the whole of the complex absorption and to determine the molecular extinction coefficient for each component band group.

In the first place, it may be noted that series of constant frequency differences occur between the centres of the band groups, and, although with the relatively small dispersive power of the spectrograph it was found to be a matter of some difficulty exactly to determine the centre of any one band group, yet the averaging of these frequency differences has enabled me to arrive at their real values with considerable accuracy.

In the second place, the whole region of absorption can be divided into three portions, namely, a less refrangible portion in which the average difference between the wave-numbers of the centres of the consecutive bands is 22·4, an extreme ultra-violet region where the average wave-number difference is about 35, and an intermediate region where combinations of these differences occur together with a third difference of about 12 *.

In the following tables are given the wave-lengths and wave-numbers of the centres of the small band groups together with the differences. In Table III. the numbers (1), (2), (3) after the differences refer to the values 22·4, 35, and 12 respectively. The molecular extinction coefficients are given at the more important points.

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* For the sake of convenience wave-numbers (reciprocals of wave-lengths) are used, expressed in four figures; that is to say, the number of waves in 1 mm.

TABLE I.—Absorption of Sulphur Dioxide in the Extreme Ultra-violet Region.

Wave-lengths in Ångströms.	Wave Numbers.	Wave-number Differences.	Molecular Extinctions.
2334	4303		
		32	
2307	4335		
		22 (1)	
2295	4357		
		34	
2277	4391		
		36	
2259	4427		
		36	
2241	4463		
		31	
2225	4494		180·3
		39	
2206	4533		551·1
		34	
2189	4567		
		36	
2172	4603		
		38	
2155	4641		
		36	
2140	4677		
		34	
2123	4711		
		36	
2107	4747		

Mean Wave-number Difference = 35·1 (2).

TABLE II.—Absorption of Sulphur Dioxide in the Near Ultra-violet Region.

Wave-lengths in Ångströms.	Wave Numbers.	Wave-number Differences.	Molecular Extinctions.
3182	3143		40·8
		24	
3157	3167		52·1
		22	
3136	3189		104·7
		24	
3112	3213		180·3
		23	
3090	3236		226·8
		25	
3066	3261		315·0
		26	
3042	3287		354·6
		22	
3022	3309		354·6
		26	
2999	3335		402·2
		23	
2978	3358		402·2
		20	
2961	*3378*	20 (Optical Centre)	*402·2*
2943	3398	22	402·2
		21	
2924	3420		402·2
		24	
2906	3441		354·6
		20	
2886	3465		354·6
		21	
2869	3485		354·6
		23	
2852	3506		354·6
		20	
2833	3529		354·6
		20	
2818	3549		354·6
2802	3569		315·0

Mean Wave-number Difference = 22·4 (1).

TABLE III.—Absorption of Sulphur Dioxide in the
Intermediate Region.

Wave-lengths in Ångströms.	Wave Numbers.	Wave-number Differences.
2789	3586	
		11 (3)
2780	3597	
		21 (1)
2764	3618	
		9 (3)
2757	3627	
		30 (2)
2734	3657	
		20 (1)
2719	3677	
		48 (2)+(3)
2685	3725	
		21 (2)
2669	3746	
		12 (1)
2661	3758	
		14 (1)
2652	3772	
		43 (2)×(2)
2621	3815	
		10 (1)
2614	3825	
		29 (2)
2594	3854	
		19 (1)
2582	3873	
		16 (3)
2572	3889	
		26 (1)
2554	3915	
		27 (1)
2537	3942	
		64 (1)+(2)
2497	4006	
		52 (2)+(3)
2464	4058	
		13 (1)
2456	4071	
		50 (2)+(3)
2427	4121	

Mean of all differences (1) = 22·4.
  „   „   „   (2) = 34·4.
  „   „   „   (3) = 12·6.

It would seem obvious from the above tables that the whole absorption region in reality consists of two principal band groups, the centre of one of which lies near $\lambda = 2960$, while the centre of the other lies beyond $\lambda = 2107$ which is the working limit of the spectrograph. In the first of these bands there is a constant difference between the wave-numbers of the centres of the sub-groups of 22·4 and in the second band there is a mean constant difference of 34·4. As regards the less refrangible band, although in Table II. five band groups have been given with a molecular extinction coefficient of 402·2, the trace of the absorption curve

shows clearly that the true optical centre lies at $\lambda = 2961$ or $1/\lambda = 3378$. According to Baly's theory this number, 3378, should be an even multiple of a fundamental band in the short-wave infra-red region. The absorption of sulphur dioxide between 3μ and 11μ has been observed by Coblentz, and the most pronounced band lies at $\lambda = 7\cdot4\mu$ or $1/\lambda = 135\cdot1$. Now $135\cdot1 \times 25 = 3377\cdot5$, which is exceedingly near to the observed ultra-violet wave-number 3378, which entirely supports Baly's contention. Moreover, Baly further postulates that the constant differences in the wave-numbers in the ultra-violet are compounded from certain basis constants which are characteristic of the molecule, and that these basis constants also determine the infra-red absorption of the molecule.

Now, the wave-numbers of the six infra-red absorption bands of sulphur dioxide observed by Coblentz * can be expressed as multiples of $96\cdot32$, as shown in Table IV.

TABLE IV.

Infra-red Absorption of Sulphur Dioxide.

Factors.	Wave Numbers.	Wave-lengths Calc.	Wave-lengths Obs.	Differences Obs.−Calc.
$9\cdot632 \times 10$	$96\cdot32$	$10\cdot38\,u$	$10\cdot37\,\mu$	$-0\cdot01$
$9\cdot632 \times 12$	$115\cdot6$	$8\cdot65$	$8\cdot7$	$+0\cdot05$
$9\cdot632 \times 14$	$134\cdot8$	$7\cdot42$	$7\cdot4$	$-0\cdot02$
$9\cdot632 \times 18$	$173\cdot3$	$5\cdot77$	$5\cdot68$	$-0\cdot09$
$9\cdot632 \times 26$	$250\cdot4$	$3\cdot99$	$3\cdot97$	$-0\cdot02$
$9\cdot632 \times 32$	$308\cdot0$	$3\cdot23$	$3\cdot18$	$-0\cdot05$

We therefore have three numbers which appear to be characteristic of the absorption of sulphur dioxide, namely, $22\cdot4$, $34\cdot4$, and $9\cdot632$, and if Baly's contention is valid these must be derived from certain basis constants characteristic of the oxygen and sulphur atoms. Now

$$22\cdot4 = \cdot2 \times 4 \times 2\cdot8 \times 10$$
$$34\cdot4 = \cdot2 \times 4 \times 4\cdot3 \times 10$$
$$9\cdot632 = \cdot2 \times 4 \times 2\cdot8 \times 4\cdot3 ;$$

and therefore it would seem that there are four basis

* Publications of the Carnegie Institution, Washington, 1905, No. 35, p. 52.

constants, 0·2, 2·8, 4, 4·3, of which the product of the first three multiplied by 10 gives a wave-number difference occurring in one ultra-violet band in sulphur dioxide, the product of another three multiplied by 10 gives a wave-number difference in the second ultra-violet band, while the product of all four determines the infra-red spectrum. Finally, the centre of the first ultra-violet band of sulphur dioxide is a multiple of the product of all four constants. On these grounds Baly's theory would lead to the expectation that the four basis constants, 0·2, 2·8, 4, 4·3, must have their origin in the oxygen and sulphur atoms. That this expectation is justified is shown by the fact that 4·3 is characteristic of the sulphur atom, since the whole of the infra-red spectrum of hydrogen sulphide can be expressed in terms of this constant, and further by the fact that the infra-red bands of oxygen can be expressed in terms of the product of 4 and 2·8, namely 11·2, as is set forth in Tables V. and VI.

TABLE V.

Infra-red Absorption of Hydrogen Sulphide.

Factors.	Wave Numbers.	Wave-lengths Calc.	Wave-lengths Obs.*	Differences Obs.−Calc.
4·3×21	90·3	11·08	10·95	−0·13
4·3×22	94·6	10·57	10·6	+0·03
4·3×23	98·9	10·11	10·08	−0·03
4·3×25	107·5	9·30	9·65	+0·35
4·3×27	116·1	8·61	8·46	−0·15
4·3×30	129·0	7·75	7·78	+0·03
4·3×33	141·9	7·05	7·12	+0·07
4·3×41	176·3	5·67	5·6	−0·07
4·3×55	236·5	4·23	4·24	+0·01

TABLE VI.

Infra-red Absorption of Oxygen.

Factors.	Wave Numbers.	Wave-lengths Calc.	Wave-lengths Obs.*	Differences Obs.−Calc.
11·2×19	212·8	4·7	4·7	0·00
11·2×28	313·6	3·19	3·2	+0·01

* Coblentz, *loc. cit.*

The differences between the calculated and observed values in Tables IV., V., and VI. show how well the theory conforms to experiments. It should, moreover, be remembered that the order of accuracy in infra-red measurements is smaller than that in the ultra-violet regions.

The whole gaseous absorption of sulphur dioxide can, therefore, be analysed as follows :—

Basis Constants : 0·2, 2·8 (oxygen), 4 (oxygen), 4·3 (sulphur).

Fundamental Frequency : (F) 0·2×2·8×4×4·3=9·632.

Infra-red Spectrum : (F) ×10, 12, 14, 18, 26, and 32.

Centre of First Ultra-violet Band : (F) ×14×25.

Constant Wave-number Difference in First Ultra-violet Band : 0·2×2·8×4×10.

Constant Wave-number Difference in Second Ultra-violet Band : 0·2×4×4·3×10.

I hope in later work to pursue this search for the basis constants characteristic of the elements.

Reference may be made to Miss Lowater's analysis of the completely resolved ultra-violet absorption spectra of sulphur dioxide, in which she determined the wave-lengths of all the absorption lines composing the sub-groups of the whole band groups [*]. Altogether 590 lines were measured by her, and these were arranged in 44 arbitrary series with constant wave-number differences. The mean of all these wave-number differences was 22·3, which is practically identical with that now found between the wave-numbers of the centres of the sub-groups over the region dealt with by Miss Lowater. Owing, however, to the great dispersion used, she did not recognize the composite nature of the spectrum dealt with above. Moreover, the intensity of her lines was estimated by inspection on the conventional basis of 10 for a very dark (absorbed) line. By such a method it is impossible to estimate the persistency of the lines, and hence the real optical centre of the resolved complex band system of the gas remained undiscovered.

Finally, as the wave-number difference 34·4 characteristic of the extreme ultra-violet region of absorption of sulphur dioxide is derived from the specific sulphur bases, it may be concluded that it is the sulphur atom of sulphur dioxide which is mainly responsible for the production of this second ultra-violet band group, a portion of which only has been observed on account of the limited transparency of quartz. By similar reasoning the oxygen atoms in the molecule must be the chief determining cause of the typical band system characteristic of the first absorption band group in the near ultra-violet region.

* Astrophys. Journal, xxxi. p. 311 (1910).

LXII. *The Ultra-violet Absorption System of Sulphur Di-oxide. By* E. C. C. BALY, *M Sc., F.R.S., Grant Professor of the University of Liverpool, and* C. S. GARRETT, *B.Sc.* *

IT was shown in the preceding paper that the ultra-violet absorption band group of gaseous sulphur dioxide can be resolved into a series of sub-groups and that constant differences exist between the wave-numbers of the centres or heads of the sub-groups.

The whole region over which absorption is exhibited can be divided into three portions, namely, that between $\lambda = 3182$ and $\lambda = 2802$ where there is a constant difference of 22·4 between the wave-numbers of twenty successive sub-groups, that between $\lambda = 2324$ and $\lambda = 2107$ where there is a constant difference of about 34·4 between the wave-numbers of fourteen sub-groups, and the intermediate portion with twenty-one sub-groups where both constant differences occur together with a third difference of about 12. It was further shown that these differences are compounded from four basis constants, 0·2, 2·8, 4, and 4·3. Further, the wave-numbers of the infra-red absorption bands of sulphur dioxide can be expressed as multiples of 96·32, which is the product of all four basis constants, while the product of 2·8 and 4 gives rise to the infra-red absorption of oxygen and 4·3 gives rise to the infra-red absorption of hydrogen sulphide.

Again, the wave-number of the centre of the less refrangible ultra-violet band of sulphur dioxide was shown to be 25 times that of the most important infra-red band of this gas, namely, $96·32 \times 14$.

Mention was also made of the accurate measurements by Miss Lowater of the component absorption lines which are associated together in the sub-groups †. Miss Lowater only investigated the region between $\lambda = 3118$ and $\lambda = 2707$; that is to say, she only measured the component lines of the less refrangible ultra-violet absorption band of sulphur dioxide. She arranged the lines in 44 arbitrary series of constant wave-number differences, and the mean of all 44 differences was 22·33. Although 42 lines were found not to fit in any of her series, it is obvious that the same constant differences occur between the individual absorption lines as was shown in the preceding paper to exist between the heads of the sub-groups.

Owing to the great dispersion used, Miss Lowater was able to measure the wave-lengths of the component absorption lines with great accuracy, and it should at once be possible to arrive at far more accurate values of the basis constants from her numbers now that the central wave-number of the less refrangible band is known.   From a knowledge of these it should also be possible to calculate the wave-number of every single component line in the absorption band group, and thus put the theory brought forward by one of us in previous papers * to a far more rigid test than has yet been possible with the compounds already studied.   Owing to the very great accuracy of Miss Lowater's measurements the wave-numbers in the following pages will be expressed in five figures, and, moreover, note must be made of the fact that her values were obtained in air and were not reduced to vacuum. This correction is necessary before any calculations from them can be made.

It was not possible to apply the general theory to sulphur dioxide until an accurate determination of the central wave-number of the ultra-violet band group had been made. As stated in the preceding paper, it has now been found that this central line lies at $\lambda = 2961$ or $1/\lambda = 33780$, but it must be remembered that the accuracy of this measurement is far below that obtained by Miss Lowater.   There are three lines of maximum intensity observed by her near this position, any one of which might be the true central line. Their wave-numbers in air are $33770\cdot3$, $33767\cdot2$, $33761\cdot2$, and the question arises as to which one of these should be selected.   The whole essence of the Bjerrum conception lies in the fact that the component absorption lines in any one band group lie symmetrically distributed about the central line, and it is a matter of simple calculation to prove that the greatest symmetry is obtained when the wave-number $33761\cdot2$ is taken as centre.   This number when reduced to vacuum becomes $33751\cdot6$, and this may be taken as the true value for the centre of the less refrangible ultra-violet absorption band of sulphur dioxide.

The relationships found by Garrett may now be dealt with, since the central wave-number is known and the basis constants calculated.   The wave-number of the most important absorption band in the short wave infra-red region of sulphur dioxide is given by $33751\cdot6/25 = 1350\cdot06$, corresponding to a wave-length of $7\cdot407\ \mu$.   Again, the least

common multiple of the basis constants is given by
$1350.06/14 = 96.433$, and, further, the wave-numbers of
the infra-red absorption bands of sulphur dioxide are
multiples of this least common multiple. This is shown
in Table I.

TABLE I.

Infra-red Absorption Spectrum of Sulphur Dioxide.

Factors.	$1/\lambda$.	λ Calc.	λ Obs.	Difference.
96.433×10	964.33	$10.37\,\mu$	$10.37\,\mu$	0.00
96.433×12	1157.20	8.64	8.7	+0.06
96.433×14	1350.06	7.41	7.4	−0.01
96.433×18	1734.79	5.76	5.68	−0.08
96.433×26	2507.26	3.99	3.97	−0.02
96.433×33	3182.29	3.14	3.18	+0.04

As regards the basis constants, Garrett has pointed out
that these are approximately 2.8, 4.3, 4, and 0.2, and that
the first and third are due to the oxygen atom, while the
second is due to the sulphur atom as shown by the infra-red
absorption wave-numbers of oxygen and hydrogen sulphide.
He showed that the wave-numbers of the infra-red absorption
bands of hydrogen sulphide may be expressed as multiples
of 4.3×10. As a matter of fact, they are still better
expressed as multiples of 4.32×10. Now, two of the most
pronounced infra-red bands are at $\lambda = 8.46\,\mu$ and $4.24\,\mu$, and
their wave-numbers, 1182 and 2359, are very nearly equal
to 43.2×27 and 43.2×55 respectively. On the other hand,
these two bands are clearly harmonic, and this suggests at
once that their wave-numbers are due to the convergence
frequency of two bases. The most probable value of the
second basis constant therefore is 2.73, and the wave-
numbers as calculated are given in Table II.

Two of the basis constants are now known accurately, and
the third, which is the product of Garrett's remaining two
constants, may be found at once, since 96.433 is the con-
vergence frequency of them all. The third, therefore, is
found to be $96.433/(4.32 \times 2.73) = 8.177$. Finally, the two
infra-red absorption bands of oxygen can be expressed in
terms of the fundamental 96.433, as shown in Table III.

TABLE II.

Infra-red Absorption Spectrum of Hydrogen Sulphide.

Factors.	$1/\lambda$.	λ Calc.	λ Obs.*	Difference.
$43{\cdot}2 \times 21$	907·2	$11{\cdot}02\,\mu$	$10{\cdot}95\,\mu$	$-0{\cdot}07$
$43{\cdot}2 \times 22$	950·4	10·52	10·6	$+0{\cdot}08$
$43{\cdot}2 \times 23$	993·6	10·06	10·08	$+0{\cdot}02$
$43{\cdot}2 \times 24$	1036·8	9·65	9·65	0·00
$43{\cdot}2 \times 27{\cdot}3$	1179·4	8·48	8·46	$-0{\cdot}02$
$43{\cdot}2 \times 30$	1296·0	7·72	7·78	$+0{\cdot}06$
$43{\cdot}2 \times 33$	1425·6	7·02	7·12	$+0{\cdot}10$
$43{\cdot}2 \times 41$	1771·2	5·65	5·6	$-0{\cdot}05$
$43{\cdot}2 \times 54{\cdot}6$	2358·8	4·24	4·24	0·00

* Coblentz, *loc. cit.*

TABLE III.

Infra-red Absorption Spectrum of Oxygen.

Factors.	$1/\lambda$.	λ Calc.	λ Obs.	Differences.
$96{\cdot}433 \times 22$	2121·53	$4{\cdot}71\,\mu$	$4{\cdot}7\,\mu$	$-0{\cdot}01$
$96{\cdot}433 \times 33$	3182·29	3·14	3·2	$+0{\cdot}06$

We have now, therefore, three basis constants, namely, 2·73, 4·32, 8·177, and from these three, combinations may be made as follows:—$8{\cdot}177 \times 2{\cdot}73 = 22{\cdot}3225$, $8{\cdot}177 \times 4{\cdot}32 = 35{\cdot}324$, and $2{\cdot}73 \times 4{\cdot}32 = 11{\cdot}794$. Of these, $22{\cdot}3225 \times 10$ is the value of the constant difference in the less refrangible ultra-violet absorption band of sulphur dioxide, $35{\cdot}324 \times 10$ is the constant difference in the more refrangible band, while $11{\cdot}794 \times 10$ is that found in the region intermediate between the two bands.

It is now possible to calculate the wave-numbers of all the lines in the less refrangible ultra-violet band of sulphur dioxide. The true wave-number of the central line is known, and also the whole band group is known to be sub-divided into a series of sub-groups with a constant difference of 223·225 between the wave-numbers of their central lines.

The general structure of the whole ultra-violet band group will be as follows :—From the general theory as laid down in the previous papers the wave-numbers of the principal lines in the band—that is to say, the heads of the sub-groups—will be given by $33.751.6 \pm n\mathrm{K}$, where K is one of the fundamental bands of the infra-red, and $n = 0, 1, 2, 3 \ldots$ It has already been found, as shown above, that K is the least common multiple of two of the basis constants, 2.73 and 8.177, and has the value 223.225. The wave-numbers of the heads of the sub-groups, therefore, will be given by $33751.6 \pm n \times 223.225$. Again, the fundamental infra-red band with the wave-number of 223.225 according to Bjerrum is itself complex and consists of a group of lines the wave-numbers of which are given by $223.225 \pm \nu_r$, where ν_r stands for the two basis constants 2.73 and 8.177. Since, however, $8.177 = 3 \times 2.73$ almost exactly, the structure of this fundamental band will be given by $223.225 \pm n \times 2.73$, where $n = 0, 1, 2, 3 \ldots$ The upper limit of n is defined by the overlapping of the band with the next infra-red band, and it is not possible to state with any exactness how far the two consecutive bands overlap. From what follows it will be seen that on the long-wave side the upper limit of n is about 44, while on the short-wave side the limit is about 37. In the fundamental infra-red band, therefore, there must be 82 lines, namely, the central line together with 44 lines on one side and 37 on the other.

The lines in the ultra-violet band are due to the combination of the central wave-number with the infra-red vibrations, and therefore the component lines of the central ultra-violet sub-group will be expressed by $33751.6 \pm n \times 2.73$. The other sub-groups are due to the combination of the wave-numbers of the lines in the fundamental infra-red band and their integral multiples with the central wave-number 33751.6. Thus the first sub-group on each side of the central sub-group will be given by $33751.6 \pm 223.225 \pm n \times 2.73$, and the second sub-group by $33751.6 \pm 2 \times 223.225 \pm n \times 2.73$, and so on.

There appear to be seven sub-groups on the less refrangible side of the central sub-group and thirteen on the more refrangible side. When each individual sub-group is considered and the wave-numbers of its component lines calculated, it appears, on comparison with Miss Lowater's list of lines, that the group is slightly asymmetric, for there are 44 lines on the less refrangible side of the centre and 37 on the more refrangible side.

The general formula, therefore, expressing the whole system of lines in the whole ultra-violet band group is $33751 \cdot 6 + p \times 223 \cdot 225 + n \times 2 \cdot 73$, where $p = -7, -6, \ldots 0 \ldots + 12, + 13$, and $n = -44, -43, \ldots 0 \ldots + 36, + 37$.

The whole band group, therefore, consists of 21 sub-groups, each containing 82 absorption lines. It is obvious from this arrangement that there must exist in the band group 82 series, each containing 21 lines with a constant difference of $223 \cdot 225$ between their wave-numbers, and we thus arrive at the true physical explanation of Miss Lowater's discovery that the lines can be arranged in series of constant wave-number differences. Miss Lowater, however, arranged her observed lines in 44 such series, but it must be remembered that there were 42 lines which she was unable to include in her series. Moreover, also the values of the mean wave-number differences she found seem to vary far more than her experimental error would permit. For example, in her 42nd series the first and nineteenth members have wave-numbers $32202 \cdot 1$ and $36231 \cdot 6$ respectively, and these give a mean wave-number difference of $223 \cdot 8$. The mean wave-number difference calculated from all 44 series is about $223 \cdot 3$, which would point to an experimental error of about $4 \cdot 5$ in the wave-numbers of each of the above two lines, an error which is very much greater than is possible from the accuracy of her work. In general it would appear that, although Miss Lowater's discovery of series of lines with constant wave-number differences is perfectly sound, yet her arrangement of the lines in these series is not the best possible.

We have calculated the wave-numbers of all the lines which the above formula establishes to be present in the whole group, and they amount to 1722. These we have arranged in the 82 series of constant difference, and compared them with Miss Lowater's observed values after reducing the latter to vacuum. The agreement between the observed and calculated values is exceedingly good, but it cannot be claimed that this agreement by itself is an absolute proof of the validity of the formula. The difference in the wave-numbers of any two consecutive lines in the spectrum is $2 \cdot 73$, and this is not much more than twice Miss Lowater's maximum experimental error, and therefore the difference between any observed line and the nearest calculated line cannot be much greater than the maximum experimental error. On the other hand, the agreement between the observed and calculated values is on the

average very much better than this, and would seem to give great support to the formula. The most important result obtained, however, is the arrangement of the observed lines into 82 series of about 21 members each, and, although no such series is complete, yet the mean wave-number differences calculated from these series are far more comparable amongst themselves than those found by Miss Lowater.

There is no need to publish the whole of the calculations, but in Table IV. are given the number of the observed lines in each of our series and the mean values of the wave-number differences that we have found, together with those of Miss Lowater's series. Our series are numbered from the central line of the sub-group in each case. Only one line has been observed which belongs to the 23rd series on the blue side, and therefore no wave-number difference can be found from this series.

The superiority of the new arrangement of the lines is manifest from Table IV. Not only are the extreme values of the differences, 223·45 and 222·94, much closer together than those of Miss Lowater's table, namely 223·9 and 222·8, but 64 per cent. of the new mean differences lie within 0·1 of the mean value, while, according to Miss Lowater's arrangement, only 34 per cent. lie within the same limits. Then, again, the means calculated from the red and blue series are the same, 223·23, and equal that calculated from the infra-red basis constants. Further, the interval between any two members of any of the new series is never greater nor less than the calculated interval by an amount greater than can be accounted for by the experimental error which Miss Lowater gives in her paper. As was shown above, Miss Lowater's arrangement of the lines can be criticised from this point of view. Every single observed line finds a place in our series between the limits $1/\lambda = 32070$ and $1/\lambda = 36646$. Six lines outside these limits have not been included, two of smaller frequency ($1/\lambda = 32065$ and 32061) and four of larger frequency ($1/\lambda = 36633\cdot3$, $36712\cdot5$, $36885\cdot1$, and 36922). The former two lines no doubt belong to the 8th sub-group on the red side noted by Garrett, while the four latter lines lie in the intermediate region between the two main absorption band groups, and therefore we have not included them since it has been shown that in this region the fundamental interval varies.

Some reference may be made to the fact that only 586 lines have been observed out of a total calculated number of 1722. This cannot be considered as an argument against the theory, for there can be no doubt that by a still further

TABLE IV.—Series of Constant Difference in the Absorption Band Group of SO$_2$.

RED SERIES.			BLUE SERIES.			Miss LOWATER'S SERIES.		
No. of Series.	No. of observed lines on each series.	Mean value of wave-number differences.	No. of Series.	No. of observed lines on each series.	Mean value of wave-number differences.	No. of Series.	No. of observed lines on each series.	Mean value of wave-number differences.
Central Series.	11	223·23	Central Series.	11	223·23			
1	7	223·18	1	4	223·25	1	8	223·1
2	8	223·32	2	13	223·24	2	14	223·3
3	8	223·28	3	8	223·27	3	13	223·4
4	9	223·23	4	5	223·10	4	9	223·5
5	10	223·15	5	9	223·22	5	9	223·9
6	8	223 27	6	7	223·28	6	13	223·2
7	7	223·16	7	10	223·28	7	10	223·1
8	11	223·25	8	6	223·25	8	10	223·1
9	6	223·27	9	12	223·24	9	10	222·9
10	10	223·21	10	6	223·26	10	8	223·4
11	8	223·22	11	9	223·21	11	12	223·4
12	8	223·05	12	9	223·30	12	8	223·1
13	7	223·19	13	6	223·37	13	12	223·0
14	7	223·26	14	8	223·36	14	13	222·9
15	10	223·21	15	4	223·14	15	15	223·0
16	5	223·19	16	9	223·28	16	12	223·4
17	6	223·40	17	4	223·00	17	11	223·5
18	11	223·36	18	8	223·30	18	6	223·4
19	8	223·18	19	6	223·22	19	11	223·1
20	7	223·12	20	3	223·27	20	9	223·0
21	9	223·21	21	7	223·21	21	10	223·0
22	4	223·10	22	7	223·25	22	12	222·8
23	10	223·26	23	1	?	23	14	223·3
24	7	223·17	24	11	223·28	24	17	223·4
25	9	223·20	25	3	223·40	25	12	223·1
26	6	223·28	26	8	223·18	26	13	223·1
27	8	223·18	27	3	223·29	27	14	223·1
28	5	223·30	28	6	223·23	28	13	223·0
29	9	223·19	29	7	223·30	29	14	223·2
30	9	223·17	30	5	222·94	30	12	222·9
31	7	223·29	31	9	223·16	31	13	223·0
32	13	223·24	32	7	223·19	32	16	223·0
33	7	223·24	33	6	223·12	33	10	223·3
34	3	223·25	34	8	223·27	34	10	223·3
35	8	223·14	35	5	223·17	35	14	223·3
36	4	223·24	36	5	223·14	36	16	223·4
37	7	223 19	37	4	223·30	37	14	223·2
38	5	223·24				38	14	223·1
39	5	223·32				39	9	223·9
40	8	223·27				40	16	223·6
41	2	223·45				41	16	223·7
42	4	223·17				42	15	223·8
43	6	223·23				43	16	223·8
44	5	223·16				44	15	223·7
						Short Series 5		223·7
Mean......		223·23	Mean......		223·23	Mean		223·26

The mean values of the wave-number differences in the various series were calculated from the observed lines in the series and are therefore comparable with those given by Miss Lowater.

improvement of the experimental conditions more lines
would be observed. One additional point may be noted,
namely, that the interval between any consecutive pair of
observed lines is never less than that calculated from the
theory.

It may fairly be claimed that the results brought forward
in this paper entirely support the theory of the relation
between infra-red and ultra-violet absorption advanced in
the previous papers, and there is little doubt of the validity
of the formula

$$13951 \cdot 6 + p \times 223 \cdot 225 + n \times 2 \cdot 73$$

for the less refrangible ultra-violet absorption band of sulphur
dioxide. The whole of this band group therefore has accu-
rately been calculated from the infra-red absorption spectra
of sulphur dioxide and hydrogen sulphide, the only additional
fact being used of the central wave-number of the ultra-
violet band which enabled the true wave-number of the
fundamental infra-red sulphur dioxide band at $7 \cdot 407 \, \mu$ to be
determined.

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LXIII. *Bessel and Neumann Functions of Equal Order and
Argument.* By John R. Airey, *M.A., D.Sc.*[*]

THE Bessel and Neumann functions $J_n(z)$, $G_n(z)$, and
$Y_n(z)$ of equal or nearly equal order and argument
occur in many physical problems, and various authors have
given formulæ expressing their behaviour under these
conditions.

Graf [†] found that when n is very large,

$$n^{\frac{1}{3}} J_n(n) = \frac{\Gamma(\frac{1}{3})}{2\pi \sqrt{3}}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

Further and more general formulæ [‡], to order $\frac{1}{n}$, were

found from the relationship between the Bessel and Neumann
functions when the argument and order are nearly equal,

and Airy's Integral, viz. in the case of the $J_n(z)$ function,

$$J_n(z) = \frac{1}{\pi}\left(\frac{6}{z}\right)^{\frac{1}{3}}\int_0^\infty \cos\left\{w^3 + (n-z)\left(\frac{6}{z}\right)^{\frac{1}{3}}w\right\}dw$$

$$= \frac{1}{3\pi}\left(\frac{6}{z}\right)^{\frac{1}{3}}\left\{\Gamma\left(\frac{1}{3}\right)\cos\frac{\pi}{6} + \frac{\rho}{1!}\Gamma\left(\frac{2}{3}\right)\cos\frac{5\pi}{6} + \frac{\rho^2}{2!}\Gamma\left(\frac{3}{3}\right)\cos\frac{9\pi}{6} + \dots\right\}, \quad (2)$$

where

$$\rho = (n-z)\left(\frac{6}{z}\right)^{\frac{1}{3}};$$

or, using De Morgan's expression * for $\displaystyle\int_0^\infty \cos(w^3 - mw)\,dw$,

$$J_{n-1}(n) = \frac{1}{2\pi\sqrt{3}}\left[\left(\frac{6}{n}\right)^{\frac{1}{3}}\Gamma\left(\frac{1}{3}\right) + \left(\frac{6}{n}\right)^{\frac{2}{3}}\Gamma\left(\frac{2}{3}\right) - \frac{1}{18}\left(\frac{6}{n}\right)^{\frac{4}{3}}\Gamma\left(\frac{1}{3}\right)\right.$$

$$\left. - \frac{1}{36}\left(\frac{6}{n}\right)^{\frac{5}{3}}\Gamma\left(\frac{2}{3}\right) + \frac{1}{1620}\left(\frac{6}{n}\right)^{\frac{7}{3}}\Gamma\left(\frac{1}{3}\right) + \frac{1}{4536}\left(\frac{6}{n}\right)^{\frac{8}{3}}\Gamma\left(\frac{2}{3}\right)\dots\right]. \quad (3)$$

The third and following terms are correctly given in (14).

When $\dfrac{z-n}{z^{\frac{1}{3}}}$ is not very small, the error in (2) becomes considerable. From Table II. in the paper † on the "Relation of Airy's Integral to the Bessel Functions," it would appear that the first root ρ_1 of $J_n(z)$ is given by

$$\rho_1 = n + 1{\cdot}1814 n^{\frac{1}{3}}. \quad \dots \quad (4)$$

From this result, ρ_1 for $J_{1000}(z)$ is 1011·8, whereas the correct value is 1018·62. It can be shown from other considerations that when λ is written for $\left(\dfrac{9\pi}{4}\right)^2$, ρ_1 is more accurately represented by

$$\rho_1 = n + \frac{(n\lambda)^{\frac{1}{3}}}{2} + \frac{3}{40}\left(\frac{\lambda^2}{n}\right)^{\frac{1}{3}}\dots \quad \dots \quad (5)$$

$$= n + 1{\cdot}841 n^{\frac{1}{3}} + 1{\cdot}017 n^{-\frac{1}{3}}.$$

This gives 1018·51 for the first root of $J_{1000}(z)$.

The function $J_n(z)$ has also been expressed asymptotically ‡ in terms of $J_{\frac{1}{3}}$ and $J_{-\frac{1}{3}}$ when the argument and the order

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* Airy, Camb. Phil. Trans. vol. viii. pp. 596–599.
† See also Lord Rayleigh, Phil. Mag. Dec. 1910.
‡ Nicholson, Phil. Mag. July 1909, p. 14. For tables of the $J_{\frac{1}{3}}$ and $J_{-\frac{1}{3}}$ functions, see Dinnik, *Archiv der Math. u. Phys.* 18 Band, S. 337, 338.

do not differ widely :

$$J_n(z) = \frac{1}{3}\sqrt{\frac{2(z-n)}{z}}\,(J_\frac{1}{3}+J_{-\frac{1}{3}}),\quad \cdot\quad \cdot\quad \cdot\quad (6)$$

the J functions of fractional order having the argument

$$\frac{2\sigma}{3}\sqrt{\frac{\sigma}{3}},\quad \text{where}\quad \sigma=-\rho.$$

From a consideration of Sommerfeld's Integral, Debye * has given the following formula for $J_n(z)$ when n and z are nearly equal. When $\frac{n}{z}=1-\epsilon$,

$$J_n(z) = \frac{1}{3\pi}\sum_{s=0}^{s=m} B_s(\epsilon z)\left(\frac{6}{z}\right)^{\frac{s+1}{3}}\Gamma\left(\frac{s+1}{3}\right)\sin(s+1)\frac{\pi}{3},\quad (7)$$

where
$$B_0(\epsilon z) = 1,$$
$$B_1(\epsilon z) = \epsilon z,$$
$$B_2(\epsilon z) = \frac{\epsilon^2 z^2}{2} - \frac{1}{20},$$
$$B_3(\epsilon z) = \frac{\epsilon^3 z^3}{6} - \frac{\epsilon z}{15},$$
$$B_4(\epsilon z) = \frac{\epsilon^4 z^4}{24} - \frac{\epsilon^2 z^2}{24} + \frac{1}{280}\cdots$$

The Bessel Function $J_n(z)$.

These results can be obtained very easily by evaluating the integral

$$J_n(z) = \frac{1}{\pi}\int_0^\pi \cos(z\sin w - nw)\,dw.\quad \cdot\quad \cdot\quad \cdot\quad (8)$$

In the case where n and z are large and equal †,

$$J_n(n) = \frac{1}{\pi}\int_0^\pi \cos n\,(\sin w - w)\,dw = \frac{1}{\pi}\int_0^\infty \cos n\left(\frac{w^3}{6} - \frac{w^5}{120} + \frac{w^7}{5040}\cdots\right)dw.$$

Changing the variable by writing

$$\frac{x}{n} = \frac{w^3}{6} - \frac{w^5}{120} + \frac{w^7}{5040}\cdots\quad \text{or}\quad \frac{6x}{n} = w^3 - \frac{w^5}{20} + \frac{w^7}{840}\cdots,$$
$$\left(\frac{6x}{n}\right)^{\frac{1}{3}} = \lambda = w - \frac{w^3}{60} + \frac{w^5}{8400}\cdots.$$

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* *Math. Annalen*, lxvii. p. 557 (1909).
† Lord Rayleigh, Phil. Mag. Dec. 1910.

Reversing this series, we get

$$w = \lambda + \frac{\lambda^3}{60} + \frac{\lambda^5}{1400} \cdots = \left(\frac{6x}{n}\right)^{\frac{1}{3}} + \frac{1}{60}\left(\frac{6x}{n}\right) + \frac{1}{1400}\left(\frac{6x}{n}\right)^5 \cdots$$

$$dw = \left[\frac{1}{3}\left(\frac{6}{n}\right)^{\frac{1}{3}} x^{-\frac{2}{3}} + \frac{1}{60}\left(\frac{6}{n}\right) + \frac{1}{840}\left(\frac{6}{n}\right)^{\frac{5}{3}} x^{\frac{2}{3}}\ldots\right] dx.$$

Hence

$$J_n(n) = \frac{1}{\pi}\int_0^\infty \left[\frac{1}{3}\left(\frac{6}{n}\right)^{\frac{1}{3}} x^{-\frac{2}{3}} + \frac{1}{60}\left(\frac{6}{n}\right) + \frac{1}{840}\left(\frac{6}{n}\right)^{\frac{5}{3}} x^{\frac{2}{3}}\ldots\right] \cos x \, dx. \quad (9)$$

But

$$\int_0^\infty x^{p-1} \cos x \, dx = \Gamma(p) \cos\frac{p\pi}{2}. \quad \cdots \quad (10)$$

Therefore

$$J_n(n) = \frac{1}{2\pi\sqrt{3}}\left[\left(\frac{6}{n}\right)^{\frac{1}{3}}\Gamma\left(\frac{1}{3}\right) - \frac{1}{420}\left(\frac{6}{n}\right)^{\frac{5}{3}}\Gamma\left(\frac{2}{3}\right) - \frac{1}{8100}\left(\frac{6}{n}\right)^{\frac{7}{3}}\Gamma\left(\frac{1}{3}\right)\right.$$
$$\left. + \frac{1}{182300}\left(\frac{6}{n}\right)^{\frac{11}{3}}\Gamma\left(\frac{2}{3}\right)\cdots\right]. \quad (11)$$

The coefficient of the last term in the bracket, $\frac{1}{182300}$, is approximate.

Even for very small values of n, this formula gives $J_n(n)$ with considerable accuracy. $J_1(1)$ is given correctly to three places of decimals, viz. 0·43995 instead of 0·44005. A closer approximation is obtained as the value of n increases, $J_6(6)$ to six, $J_{48}(48)$ to nine, and $J_{750}(750)$ to fourteen places of decimals.

n.	$J_n(n)$.		
6	0·2458	37	
48	0·1230	7185	7
750	0·0492	3244	5583 97

Although n must be an integer in (8), the formulæ (11), (13), and (14) appear to be valid even when n does not fulfil this condition.

When z and n are nearly equal, say $z = n + \kappa$,

$$J_n(z) = \frac{1}{\pi}\int_0^\infty \cos\left[z(\sin w - w) + \kappa w\right] dw$$
$$= \frac{1}{\pi}\int_0^\infty \cos z(\sin w - w)\cos \kappa w \, dw - \frac{1}{\pi}\int_0^\infty \sin z(\sin w - w)\sin \kappa w \, dw. \quad (12)$$

Taking the first integral,

$$\frac{1}{\pi}\int_0^\infty \cos\kappa w \cos z(\sin w - w)\,dw = \frac{1}{\pi}\int_0^\infty \left(1 - \frac{\kappa^2 w^2}{2}\cdots + \frac{\kappa^4 w^4}{24}\cdots\right)\cos z(\sin w - w)\,dw$$

As in the preceding example,

$$\frac{1}{\pi}\int_0^\infty \cos z(\sin w - w)\,dw = \frac{1}{2\pi\sqrt{3}}\left[\left(\frac{6}{z}\right)^{\frac{1}{3}}\Gamma\left(\frac{1}{3}\right) - \frac{1}{280}\left(\frac{6}{z}\right)^{\frac{5}{3}}\Gamma\left(\frac{5}{3}\right) - \cdots\right].$$

Similarly,

$$-\frac{1}{\pi}\int_0^\infty \frac{\kappa^2 w^2}{2}\cos z(\sin w - w)\,dw = \frac{1}{2\pi\sqrt{3}}\left[\frac{\kappa^2}{24}\left(\frac{6}{z}\right)^{\frac{5}{3}}\Gamma\left(\frac{5}{3}\right) + \frac{\kappa^2}{288}\left(\frac{6}{z}\right)^{\frac{7}{3}}\Gamma\left(\frac{7}{3}\right)\cdots\right]$$

and so on.

The terms arising out of the second integral of (12) can be found in a similar way from

$$\int_0^\infty x^{p-1}\sin x\,dx = \Gamma(p)\sin\frac{p\pi}{2}.$$

Collecting the terms, the following expression for $J_n(z)$ is obtained. when $z = n + \kappa$:—

$$J_n(z) = \frac{1}{2\pi\sqrt{3}}\left[B_0\left(\frac{6}{z}\right)^{\frac{1}{3}}\Gamma\left(\frac{1}{3}\right) + B_1\left(\frac{6}{z}\right)^{\frac{2}{3}}\Gamma\left(\frac{2}{3}\right) - \frac{1}{3}B_3\left(\frac{6}{z}\right)^{\frac{4}{3}}\Gamma\left(\frac{1}{3}\right)\right.$$

$$-\frac{2}{3}B_4\left(\frac{6}{z}\right)^{\frac{5}{3}}\Gamma\left(\frac{2}{3}\right) + \frac{4}{9}B_6\left(\frac{6}{z}\right)^{\frac{7}{3}}\Gamma\left(\frac{1}{3}\right) + \frac{10}{9}B_7\left(\frac{6}{z}\right)^{\frac{8}{3}}\Gamma\left(\frac{2}{3}\right)$$

$$\left.-\frac{28}{27}B_9\left(\frac{6}{z}\right)^{\frac{10}{3}}\Gamma\left(\frac{1}{3}\right)\cdots\right], \qquad \cdots \cdots \quad (13)$$

where

$$B_0 = 1,$$

$$B_1 = \kappa,$$

$$B_3 = \frac{\kappa^3}{6} - \frac{\kappa}{15},$$

$$B_4 = \frac{\kappa^4}{24} - \frac{\kappa^2}{24} + \frac{1}{280},$$

$$B_6 = \frac{\kappa^6}{720} - \frac{7\kappa^4}{1440} + \frac{\kappa^2}{288} - \frac{1}{3600},$$

$$B_7 = \frac{\kappa^7}{5040} - \frac{\kappa^5}{900} + \frac{19\kappa^3}{12600} - \frac{13\kappa}{31500},$$

$$B_9 = \frac{\kappa^9}{362880} - \frac{\kappa^7}{30240} + \frac{71\kappa^5}{604800} - \frac{121\kappa^3}{907200} + \frac{7939\kappa}{232848000}\cdots$$

In the important case where the order of the function is $n-1$ and the argument n,

$$J_{n-1}(n) = \frac{1}{2\pi\sqrt{3}}\left[\left(\frac{6}{n}\right)^{\frac{1}{3}}\Gamma\left(\frac{1}{3}\right) + \left(\frac{6}{n}\right)^{\frac{2}{3}}\Gamma\left(\frac{2}{3}\right) - \frac{1}{30}\left(\frac{6}{n}\right)^{\frac{4}{3}}\Gamma\left(\frac{1}{3}\right)\right.$$
$$- \frac{1}{420}\left(\frac{6}{n}\right)^{\frac{5}{3}}\Gamma\left(\frac{2}{3}\right) - \frac{1}{8100}\left(\frac{6}{n}\right)^{\frac{7}{3}}\Gamma\left(\frac{1}{3}\right)$$
$$\left. + \frac{23}{113400}\left(\frac{6}{n}\right)^{\frac{8}{3}}\Gamma\left(\frac{2}{3}\right) + \frac{947}{74844000}\left(\frac{6}{n}\right)^{\frac{10}{3}}\Gamma\left(\frac{1}{3}\right)\dots\right]. \quad (14)$$

The numerical values occurring in the above formulæ are

$$\log\Gamma\left(\frac{1}{3}\right) = 0\cdot42796\ 27493\ 1426 : \Gamma\left(\frac{1}{3}\right) = 2\cdot67893\ 85347\ 077$$

$$\log\Gamma\left(\frac{2}{3}\right) = 0\cdot13165\ 64916\ 8402 : \Gamma\left(\frac{2}{3}\right) = 1\cdot35411\ 79394\ 264$$

The formulæ (11) and (14) give the values of $J_n(n)$ and $J_{n-1}(n)$, and the recurrence formula $J_{n-1} - \frac{2n}{z}J_n + J_{n+1} = 0$ enables one to find functions of higher or lower order. In this way the behaviour of $J_n(z)$ in the neighbourhood of its first root can be investigated. For example, in calculating the first root of $J_{100}(z)$, $J_{109}(109)$ and $J_{108}(109)$ are first found, and from these values the functions $J_{107}(109)$, &c., down to $J_{100}(109)$ as follows :—

n.	$J_n(109)$.	n.	$J_n(109)$.
109	0·093639	104	0·134966
108	0·111472	103	0·115672
107	0·127260	102	0·083643
106	0·138378	101	0·040870
105	0·141879	100	−0·007901

Bessel's addition theorem * for the J functions, viz.,

$$J_n(z+h) = \left(\frac{z+h}{z}\right)^n\left[J_n(z) - \frac{\alpha}{1!}J_{n+1}(z) + \frac{\alpha^2}{2!}J_{n+2}(z)\dots\right], \quad (15)$$

where $\qquad\qquad \alpha = \frac{h(2z+h)}{2z}$,

then gives the value of h, $(-0\cdot164\dots)$, which makes $J_n(z+h) = 0$ when $n = 100$ and $z = 109$. The first root of $J_{100}(z)$ is therefore $108\cdot836$. By the same method, and by

* *Abhandlungen der Berliner Akademie*, 1824 ; Nielsen, 'Theorie der Cylinderfunktionen,' S. 266.

the one indicated at the end of this paper, the first roots of $J_{10}(z)$ and $J_{1000}(z)$ are 14·4755 and 1018·62.

The value of $J_n(n+\kappa)$ can be found directly from (13) when κ is larger than unity, if n is large. For example *, $J_{18}(20)=0\cdot25109$. This result is more easily and accurately obtained from $J_{19}(20)$ and $J_{20}(20)$.

The Neumann Functions $G_n(z)$ *and* $Y_n(z)$.

The function †

$$G_n(z) = \frac{\pi}{2}\left[\frac{J_{-n}(z) - \cos n\pi J_n(z)}{\sin n\pi}\right].$$

Substituting

$$J_{-n}(n) = -\frac{1}{\pi\sqrt{3}}\left[\left(\frac{6}{n}\right)^{\frac{1}{3}}\cos\pi\left(\frac{2}{3}+n\right) - \frac{1}{420}\left(\frac{6}{n}\right)^{\frac{5}{3}}\Gamma\left(\frac{2}{3}\right)\cos\pi\left(\frac{10}{3}+n\right)\ldots\right], \quad (16)$$

and making n integral, we get

$$G_n(n) = \frac{1}{4}\left[\left(\frac{6}{n}\right)^{\frac{1}{3}}\Gamma\left(\frac{1}{3}\right) + \frac{1}{420}\left(\frac{6}{n}\right)^{\frac{5}{3}}\Gamma\left(\frac{2}{3}\right) - \frac{1}{8100}\left(\frac{6}{n}\right)^{\frac{7}{3}}\Gamma\left(\frac{1}{3}\right)\right.$$
$$\left. - \frac{1}{182300}\left(\frac{6}{n}\right)^{\frac{11}{3}}\Gamma\left(\frac{2}{3}\right) + \ldots\right]. \quad (17)$$

The following asymptotic series represents $G_n(z)$ when the argument $z=n+\kappa$:—

$$G_n(z) = \frac{1}{4}\left[B_0\left(\frac{6}{z}\right)\Gamma\left(\frac{1}{3}\right) - B_1\left(\frac{6}{z}\right)^{\frac{2}{3}}\Gamma\left(\frac{2}{3}\right) - \frac{1}{3}B_3\left(\frac{6}{z}\right)^{\frac{4}{3}}\Gamma\left(\frac{1}{3}\right)\right.$$
$$+ \frac{2}{3}B_4\left(\frac{6}{z}\right)^{\frac{5}{3}}\Gamma\left(\frac{2}{3}\right) + \frac{4}{9}B_6\left(\frac{6}{z}\right)^{\frac{7}{3}}\Gamma\left(\frac{1}{3}\right) - \frac{10}{9}B_7\left(\frac{6}{z}\right)^{\frac{8}{3}}\Gamma\left(\frac{2}{3}\right)$$
$$\left. - \frac{28}{27}B_9\left(\frac{6}{z}\right)^{\frac{10}{3}}\Gamma\left(\frac{1}{3}\right) + \ldots\right], \quad \ldots \ldots \ldots \quad (18)$$

the coefficients B_0, B_1, &c., having the same meaning as before. In the special case where n is the argument and $n-1$ the order of the function,

$$G_{n-1}(n) = \frac{1}{4}\left[\left(\frac{6}{n}\right)^{\frac{1}{3}}\Gamma\left(\frac{1}{3}\right) - \left(\frac{6}{n}\right)^{\frac{2}{3}}\Gamma\left(\frac{2}{3}\right) - \frac{1}{30}\left(\frac{6}{n}\right)^{\frac{4}{3}}\Gamma\left(\frac{1}{3}\right) + \frac{1}{420}\left(\frac{6}{n}\right)^{\frac{5}{3}}\Gamma\left(\frac{2}{3}\right)\right.$$
$$- \frac{1}{8100}\left(\frac{6}{n}\right)^{\frac{7}{3}}\Gamma\left(\frac{1}{3}\right) - \frac{23}{113400}\left(\frac{6}{n}\right)^{\frac{8}{3}}\Gamma\left(\frac{2}{3}\right)$$
$$\left. + \frac{947}{74844000}\left(\frac{6}{n}\right)^{\frac{10}{3}}\Gamma\left(\frac{1}{3}\right)\ldots\right]. \quad \ldots \ldots \ldots \quad (19)$$

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* Phil. Mag. July 1909, p. 17.
† Gray & Mathews, 'Bessel Functions,' p. 242.

The following values calculated from these formulæ may be compared with those * found from $G_0(n)$ and $G_1(n)$ by means of the recurrence formula, $G_{n+1} = \dfrac{2n}{z} G_n - G_{n-1}$.

$n.$	$G_n(n).$	$G_{n-1}(n).$
7	0·636755	0·313070
8	0·608951	0·314261
9	0·585445	0·314077
10	0·565195	0·313060
11	0·547485	0·311526
12	0·531806	0·309676
13	0·517782	0·307632

$G_{n-1}(n)$ has a maximum value near $n = 8\cdot316$.

To find the first root of $G_{100}(z)$, the values of $G_{104}(104)$ and $G_{103}(104)$ are calculated, and from these results functions of higher and lower orders are readily obtained.

$n.$	$G_n(104).$	$n.$	$G_n(104).$
100	0·025594	104	0·258794
101	0·091802	105	0·309836
102	0·152713	106	0·366837
103	0·207751	107	0·437957

Bessel's formula (15) is equally applicable to the G and Y functions, giving finally 104·380, as the first root of $G_{100}(z)$.

Since the Neumann function † $Y_n(z)$ is given by

$$Y_n(z) = (\log 2 - \gamma)J_n(z) - G_n(z), \qquad . \quad . \quad (20)$$

expressions for $Y_n(n)$ and $Y_{n-1}(n)$ can be found by substituting (11) and (17) or (14) and (19) in (20). The first root of $Y_{100}(z)$ calculated as in the previous examples is 104·133.

It can be shown that ρ_m, the mth root of $J_n(z)$, is given very approximately by the formula

$$\rho_m = n \sec \phi, \qquad . \quad . \quad . \quad . \quad . \quad (21)$$

where $\qquad \tan \phi - \phi = \dfrac{(4m-1)\pi}{4n}. \qquad . \quad . \quad . \quad . \quad (22)$

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* British Association Report: Calculation of Mathematical Tables, 1914.

† Gray & Mathews, 'Bessel Functions,' pp. 14, 242.

This formula and others giving still closer values of the roots are especially useful when m is small in comparison with n. The formulæ given by McMahon [*] and others for the roots of $J_n(z)$, $Y_n(z)$ are limited in their application, and cannot be employed in finding the earlier roots of $J_n(z)$, &c., when n is large. Similar expressions are found for the roots of the two Neumann functions.

LXIV. *Divergence and Curl in a Vector Field in terms of curvature and tortuosity.* By V. KARAPETOFF [†].

THE usual expressions for divergence and curl, in Cartesian coordinates, convey a somewhat indirect picture of the physical nature of these quantities, particularly to the beginner. The expressions given below are based directly upon the characteristics of a field near a given point, namely, the geometric shape of the lines of force, and the rate of change of the field density along a line of force and in the directions perpendicular to it. No fixed origin of coordinates or projections with respect to this origin are introduced into the discussion. For the sake of simplicity, and as a sort of introduction to the method, a two-dimensional field is considered first.

1. TWO-DIMENSIONAL FIELD.

Let AB, A′B′, A″B″ (fig. 1) represent lines of force of a vector field in the vicinity of a point O. Let these lines lie in the plane of the paper, and let all the lines of the field lie in parallel planes, so that the field may be called two-dimensional. The field at and near point O is determined by the following quantities and characteristics :—

(1) The magnitude and the direction of the flux density D at O.
(2) The scalar rate of change of flux density, $\partial D/\partial s$, along the line of force AB.
(3) The scalar rate of change of flux density, $\partial D/\partial n$, along the normal to AB.
(4) The radius of curvature, PO $= \rho$, of AB.
(5) The radius of spread, QO $=$ R, at O.
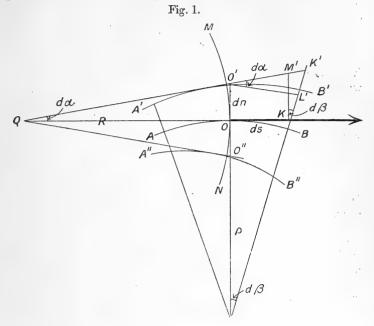
The latter radius is defined as the radius of curvature of the curve MN, orthogonal to the lines of force at and near point O. The centre of spread is denoted in the figure by Q.

Fig. 1.

Curve MN is not necessarily an equipotential line, because the discussion is not limited to a lamellar field. The field is assumed in the general case to be neither lamellar nor solenoidal.

1 a. *Divergence in two dimensions.*

Let $dn = OO'$ be an element of the normal to the line of force; then the flux through OO', for unit thickness of the field in the direction perpendicular to the plane of the paper, is $D\,dn$. By definition, divergence is the limit of the ratio of the excess flux through an infinitesimal volume to the volume itself; thus

$$\text{div D} = \frac{\frac{\partial}{\partial s}(D\,dn)ds}{dn\,ds}, \quad \cdots \quad (1)$$

or

$$\text{div D} = \frac{\partial D}{\partial s} + D\frac{\frac{\partial}{\partial s}(dn)}{dn}. \quad \cdots \quad (2)$$

Since we are dealing with infinitesimal dimensions, OB may be taken to be a straight line, and O'B' coincides with the tangent O'K'. Drawing a line O'L' parallel to OB (or to OK) triangle O'K'L' is obtained, in which angle $d\alpha$ represents the rate of increase of dn with s, or

$$d\alpha = \frac{\partial(dn)}{\partial s}.$$

But the same angle obtains at Q, where $d\alpha = dn/R$, so that we have

$$\frac{\partial(dn)}{\partial s} = \frac{dn}{R}.$$

Substituting this expression into eq. (2) we finally obtain

$$\operatorname{div} D = \frac{\partial D}{\partial s} + \frac{D}{R}. \quad \cdots \quad (3)$$

In other words, the divergence at a point in a two-dimensional field depends only upon the flux density, the rate of change of this density along the tangent, and the radius of spread. The divergence is independent of the radius of curvature of the field and of the rate of increase of the flux density along the normal.

Special cases: (a) *Solenoidal flux.*—For such a flux $D\,dn$ is the same at OO' as at BB'; thus,

$$\frac{\partial(D\,dn)}{\partial s} = 0. \quad \cdots \quad (4)$$

or
$$D\,dn = \text{const.}$$

This means that for any two points, 1 and 2, along a line of force,

$$\frac{D_1}{D_2} = \frac{dn_2}{dn_1}.$$

Eq. (3) shows shows that $\operatorname{div} D = 0$, when

$$\frac{\partial D}{\partial s} + \frac{D}{R} = 0. \quad \cdots \quad (5)$$

By analogy with the potential function for a lamellar flux, a *flux function*, ψ, may be introduced for the solenoidal flux. This function is defined by the equation

$$D = \frac{\partial \psi}{\partial n}, \quad \cdots \quad (5\,a)$$

and the existence of such a function is a condition for the

flux being solenoidal. We have $\mathrm{D}\,dn = d\psi$, and since $d\psi$ is independent of s,

$$\frac{\partial(d\psi)}{\partial s} = 0. \quad . \quad . \quad . \quad . \quad . \quad (5\,b)$$

Eq. (5) becomes

$$\frac{\partial^2\psi}{\partial s\,\partial n} + \frac{1}{R}\frac{\partial\psi}{\partial n} = 0. \quad . \quad . \quad . \quad (5\,c)$$

The physical meaning of function ψ is as follows: the numerical value of ψ is equal to the flux comprised between the line of force under consideration and some other arbitrary line of force selected as a reference; the flux is understood to be per unit of thickness in the direction perpendicular to the plane of the paper.

(b) *Lines of force are parallel near* O.—In this case $R = \infty$, and

$$\operatorname{div} \mathrm{D} = \frac{\partial \mathrm{D}}{\partial s}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

(c) *Lamellar field.*—Let ϕ be the potential function. Then

$$\mathrm{D} = \frac{\partial\phi}{\partial s}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and eq. (3) becomes

$$\operatorname{div} \mathrm{D} = \frac{\partial^2\phi}{\partial s^2} + \frac{1}{R}\frac{\partial\phi}{\partial s}; \quad . \quad . \quad . \quad . \quad (8)$$

this is equivalent to Poisson's equation in rectangular co-ordinates.

(d) *Solenoidal lamellar field* :

$$\frac{\partial^2\phi}{\partial s^2} + \frac{1}{R}\frac{\partial\phi}{\partial s} = 0. \quad . \quad . \quad . \quad . \quad (9)$$

This equation is equivalent to Laplace's equation in rectangular coordinates.

1 b. *Curl in two dimensions.*

By definition, the curl of D at point O (fig. 1) is the limit of the ratio of the line integral of D taken (say) along OBB'O'O to the area enclosed by that path. But the line integrals along BB' and OO' vanish because the field there is perpendicular to the path, so that

$$\operatorname{curl} \mathrm{D} = \frac{\dfrac{\partial}{\partial n}(\mathrm{D}\,ds)dn}{dn\,ds} = \frac{\partial \mathrm{D}}{\partial n} + \frac{\mathrm{D}}{ds}\frac{\partial(ds)}{\partial n}. \quad . \quad (10)$$

To express the last term through the radius of curvature, we draw KM′ parallel to OO′. Angle K′KM′ is a measure for the rate of increase of ds along the normal, or

$$d\beta = \frac{\partial(ds)}{\partial n}.$$

But the same angle $d\beta$ obtains at the centre of curvature P, where

$$d\beta = \frac{ds}{\rho}.$$

Thus

$$\frac{\partial(ds)}{\partial n} = \frac{ds}{\rho}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Substituting this value into eq. (10) we get

$$\operatorname{curl} D = \frac{\partial D}{\partial n} + \frac{D}{\rho}. \quad . \quad . \quad . \quad . \quad (12)$$

It will thus be seen that the curl at a point in a two-dimensional field depends only upon the flux density, the rate of change of this density along the normal, and the radius of curvature of the field. The curl is independent of the rate of increase of the flux density in the direction of the field and is also independent of the radius of spread.

Examining expression (12) for the curl together with eq. (3) for the divergence, it will be seen that these two expressions together contain all the five characteristics enumerated at the beginning of the article. Moreover, expressions (1), (2), and (3) are formally similar to eqs. (10) and (12), and this fact perhaps helps to see why in vector analysis the same Hamiltonian operator is used for both divergence and curl.

Special cases : (a) *Lamellar flux.*—For such a flux there is a potential function ϕ such that $D = d\phi/ds$. In eq. (10), $D\,ds = d\phi$, and since $d\phi$ between two equipotential surfaces is independent of n,

$$\frac{\partial(D\,ds)}{\partial n} = 0$$

or

$$\operatorname{curl} D = 0.$$

Eq. (12) becomes

$$\frac{\partial D}{\partial n} + \frac{D}{\rho} = 0, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which is the condition for the flux being solenoidal. Introducing the potential function we get

$$\frac{\partial^2\phi}{\partial n\,\partial s} + \frac{1}{\rho}\frac{\partial\phi}{\partial n} = 0. \quad \ldots \quad (14)$$

This expression is analogous to equation (5 c) for the solenoidal flux.

(b) *Lines of force are parallel near* O.—In this case $\rho = \infty$ and

$$\operatorname{curl} D = \frac{\partial D}{\partial n}. \quad \ldots \quad (15)$$

(c) *Solenoidal flux.*—Introducing again the flux function ψ we get

$$\operatorname{curl} D = \frac{\partial^2\psi}{\partial n^2} + \frac{1}{\rho}\frac{\partial\psi}{\partial n}. \quad \ldots \quad (16)$$

This is analogous to Poisson's expression for the divergence of a lamellar field, in the form (8).
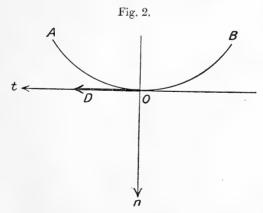
(d) *Solenoidal lamellar field*:

$$\frac{\partial^2\psi}{\partial n^2} + \frac{1}{\rho}\frac{\partial\psi}{\partial n} = 0. \quad \ldots \quad (17)$$

This corresponds to Laplace's equation in the form (9).

The curl of a two-dimensional field is a solenoidal vector, because its lines of force are straight lines, and the flux density remains the same from layer to layer of the original field. Thus, in expression (3) both terms on the right-hand side are equal to zero separately.

2. Three-Dimensional Field.

Fig. 2.

A three-dimensional field at and near a point O (figs. 2, 3, and 4) may be described with reference to the following

three mutually perpendicular directions which are defined by the line of force AB through O :—

(1) The tangent t to the line of force ;
(2) The principal normal n to the same curve ;
(3) The binormal b of the same curve.

Fig. 3.
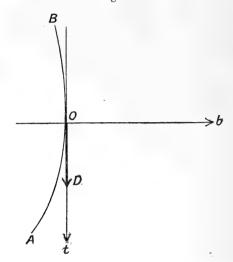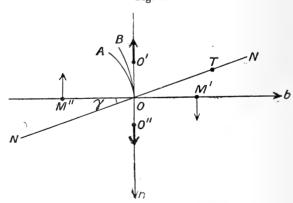
Fig. 4.

These three axes determine the following three planes :—

(1) The osculating plane, tn, in which fig. 2 is drawn ;
(2) The rectifying plane, tb, in which fig. 3 is drawn ;
(3) The normal plane, nb, in which fig. 4 is drawn.

The curves drawn in these figures represent, therefore, the projections of the line of force AB upon these planes. The field is determined by quantities similar to those mentioned above for the two-dimensional field, only a greater number is required to account for the changes in three dimensions.

2 a. *Divergence in three dimensions.*

Consider an infinitesimal tube of flux near O, of a rectangular cross-section, having a width dn in the direction of the principal normal, and a width db in the direction of the binormal. The flux comprised in the tube is $D\, dn\, db$, and the volume of the tube of a length ds in the direction of D is $dn\, db\, ds$. Thus, by definition

$$\operatorname{div} D = \frac{\dfrac{\partial}{\partial s}(D\, dn\, db)ds}{dn\, db\, ds} , \quad \cdot \quad \cdot \quad \cdot \quad (18)$$

or

$$\operatorname{div} D = \frac{\partial D}{\partial s} + D\frac{\dfrac{\partial}{\partial s}(dn)}{ds} + D\frac{\dfrac{\partial}{\partial s}(db)}{ds} \quad \cdot \quad \cdot \quad (19)$$

The last two terms on the right-hand side are similar to those in eq. (2), and by a similar reasoning we obtain :

$$\operatorname{div} D = \frac{\partial D}{\partial s} + \frac{D}{R_0} + \frac{D}{R_r}, \quad \cdot \quad \cdot \quad \cdot \quad (20)$$

where R_0 is the radius of spread in the osculating plane and R_r is that in the rectifying plane [*].

It will thus be seen that the divergence does not depend upon the rate of change of flux density in the normal plane.

For a solenoidal flux,

$$\frac{\partial D}{\partial s} + \frac{D}{R_0} + \frac{D}{R_r} = 0. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (21)$$

For a solenoidal and lamellar flux, if ϕ is the potential function,

$$\frac{\partial^2 \phi}{\partial s^2} + \left(\frac{1}{R_0} + \frac{1}{R_r}\right)\frac{\partial \phi}{\partial s} = 0, \quad \cdot \quad \cdot \quad \cdot \quad (22)$$

which is equivalent to Laplace's equation in the usual form.

---

[*] A similar formula may be deduced by considering directly the radii of curvature of a surface orthogonal to the flux. See W. v. Ignatowsky, *Die Vectoranalysis*, 1909, vol. i. p. 84.

2 b. *Curl in three dimensions.*

The vector of a curl, generally speaking, is not normal to the original vector D. It is therefore convenient to deduce expressions for the projections of the curl upon the three axes of coordinates t, n, and b, referred to above. The expressions so obtained may in some cases give a better insight into the physical nature of the curl than the usual expressions of its projections upon a fixed system of coordinates.

(a) *The component of the curl along the binormal.*—This component is perpendicular to the projection of the line of force shown in fig. 2 : its value may be deduced in exactly the same way as is done for the two-dimensional field above. We thus get an expression similar to eq. (12):

$$(\operatorname{curl} D)_b = \frac{\partial D}{\partial n} + \frac{D}{\rho} . \quad . \quad . \quad . \quad (23)$$

The subscript b indicates a component of the curl along the binormal, and ρ is the radius of curvature of the line of force at O. This component of the curl represents the whole curl in a two-dimensional field.

(b) *The component of the curl along the normal.*—This component is perpendicular to the projection of the line of force shown in fig. 3. By analogy with eq. (23) we have

$$(\operatorname{curl} D)_n = \frac{\partial D}{\partial b} + \frac{D}{\tau} , \quad . \quad . \quad . \quad (24)$$

where τ is the radius of tortuosity * of the line of force at O.

(c) *The component of the curl in the direction of vector D itself.*—This component of the curl is perpendicular to the projection of the line of force shown in fig. 4. Since it is not possible to speak of the curvature of the line of force in the plane of fig. 4, no expression similar to eqs. (23) and (24) can be written for this component of the curl. It is convenient to apply to this plane the usual expression for the component of a curl in Cartesian coordinates. Using the directions of b and n as the axes of coordinates, we get

$$(\operatorname{curl} D)_t = \frac{\partial D_n}{\partial b} - \frac{\partial D_b}{\partial n} , \quad . \quad . \quad . \quad (25)$$

---

* The term tortuosity is used in this article in place of the more usual term torsion, in order to avoid a possible ambiguity in application, for example, to the theory of elasticity, where the term torsion has a meaning of its own.

where D_n and D_b are the projections of the vector D upon b and n, at points near O.

Consider points O′ and O″ (fig. 4) infinitely close to O, and situated upon the n-axis. At these points the total components of D upon the normal plane of the vector at O are directed along the n-axis, as is shown by heavy arrow-heads. This is because the osculating planes at O′ and O″ form an infinitesimal angle with that at O, and D has no projection upon the n–b plane at O. Thus, the component D_b at O′ or O″ is an infinitesimal of the second order as compared with the component D_n which is an infinitesimal of the first order.

Therefore, in eq. (25) we may put

$$\frac{\partial D_b}{\partial n}=0, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (26)$$

and consequently

$$(\operatorname{curl} D)_t=\frac{\partial D_n}{\partial b}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (27)$$

Consider now points M′ and M″ infinitely close to O, and situated upon the b-axis. If the component of the curl according to eq. (27) has a finite value, the components D_n at these points must be in opposite directions, because $D_n=0$ at point O. Thus, the existence of a curl in the direction of the vector itself is due to a lack of symmetry of the field with respect to the osculating plane nt. A two-dimensional flux is always symmetrical with respect to its plane, and consequently there is no component of the curl in the direction of the vector itself [*].

Take a point T in the plane nb, with coordinates dn and db. The component of the vector D at this point, parallel to n, is

$$D_n=\frac{\partial D}{\partial b}\,db+\frac{\partial D_n}{\partial n}dn. \quad \cdot \quad \cdot \quad \cdot \quad (28)$$

---

[*] The foregoing expressions for the components of a curl may be also derived as a specific case from the general expressions for "rotation" in curvilinear orthogonal coordinates. See, for example, A. E. H. Love, 'Mathematical Theory of Elasticity,' second edition, pp. 54–56. It is believed, however, that the simple derivation given above is better adapted for the needs of physicists, and perhaps gives more insight into the nature of curl. See also J. Spielrein, " Geometrisches zur elektrischen Festigkeitsrechnung," *Archiv für Elektrotechnik*, vol. iv. p. 78 (1915).

Let point T be so selected that $D_n = 0$.   Then

$$\frac{\partial D_n}{\partial b} db + \frac{\partial D_n}{\partial n} dn = 0,$$

   or

$$\frac{dn}{db} = \tan \gamma = - \frac{\partial D_n / \partial b}{\partial D_n / \partial n}. \quad . \quad . \quad . \quad (29)$$

In other words, the points for which $D_n = 0$ determine a plane NN inclined by an angle γ to the rectifying plane. This angle is determined by eq. (29) and characterizes the amount by which the flux is *skewed*.   Without tortuosity, that is in a two-dimensional field, $\gamma = 0$ and plane NN coincides with bt.

In the preceding discussion, the derivative $\partial D_b / \partial b$ is left out of consideration, because it does not enter in the expression for the curl.   The flux may spread to any degree in the rectifying plane, without affecting the component of the curl in the direction of vector D.

SUMMARY.

Divergence.

In two dimensions: div $D = \dfrac{\partial D}{\partial s} + \dfrac{D}{R}$;

In three dimensions : div $D = \dfrac{\partial D}{\partial s} + D \left(\dfrac{1}{R_0} + \dfrac{1}{R_r} \right)$.

Curl.

In two dimensions : curl $D = \dfrac{\partial D}{\partial n} + \dfrac{\dot{D}}{\rho}$;

In three dimensions the projections of the curl are as follows :—

   along the binormal, (curl $D)_b = \dfrac{\partial D}{\partial n} + \dfrac{D}{\rho}$;

   along the normal, (curl $D)_n = \dfrac{\partial D}{\partial b} + \dfrac{D}{\tau}$;

   along the vector itself, or along the tangent,

$$(\text{curl } D)_t = \frac{\partial D_n}{\partial b}.$$

LXV. *On Wave-Patterns due to a Travelling Disturbance.* By Prof. H. LAMB, *F.R.S.**

1. THE procedure of a former paper † may be adapted to the case of propagation in two dimensions, as when a pressure-point advances over the surface of water. Although nothing very novel is to be looked for in the way of results, the generalized treatment of a somewhat intricate problem may be acceptable.

The method, it may be recalled, depends ultimately on integrals of the type

$$\int \frac{F(z)}{f(z)} e^{izx} dz, \quad \ldots \quad \ldots \quad (1)$$

taken round suitable contours. The functions $F(z), f(z)$ are usually algebraic, and $f(z)$ has one or more simple roots of the form $\kappa + i\mu_1$, where κ is positive and μ_1, which depends on an assumed frictional coefficient, is in the end taken to be infinitesimal. For simplicity of statement it is assumed for the most part that there is only one root of $f(z)$ of the above type.

First suppose that x is positive. We put $z = k + im$, and integrate round the boundary of the infinite quadrant in which k, m are positive. If $\mu_1 > 0$, this region contains the singular point $\kappa + i\mu_1$, which must be excluded. Thus

$$\int_0^\infty \frac{F(k)}{f(k)} e^{ikx} dk = \frac{2\pi i F(\kappa + i\mu_1)}{f'(\kappa + i\mu_1)} e^{i\kappa x - \mu_1 x} + i \int_0^\infty \frac{F(im)}{f(im)} e^{-mx} dm. \quad (2)$$

The latter integral diminishes rapidly with increasing x. In particular, if

$$\frac{i F(im)}{f(im)} = A + Bm + Cm^2 + \ldots, \quad \ldots \quad (3)$$

its asymptotic value is

$$\frac{A}{x} + \frac{B}{x^2} + \frac{1.2\,C}{x^3} + \ldots \quad \ldots \quad \ldots \quad (4)$$

Hence, when $\mu_1 \to 0$, we have, for sufficiently large values of x,

$$\int_0^\infty \frac{F(k)}{f(k)} e^{ikx} dk = \frac{2\pi i F(\kappa)}{f'(\kappa)} e^{i\kappa x}. \quad \ldots \quad \ldots \quad (5)$$

If, on the other hand, $\mu_1 < 0$, the first term on the right-hand side of (2) is absent, since the region considered has now no singular point. We have then

$$\int_0^\infty \frac{\mathrm{F}(k)}{f(k)} e^{ikx} dk = 0, \quad \cdots \cdots \quad (6)$$

with the same approximation as in (5).

Next, suppose x to be negative. We now take as our contour that of the infinite quadrant for which k is positive and m negative. Thus, if $\mu_1 < 0$,

$$\int_0^\infty \frac{\mathrm{F}(k)}{f(k)} e^{ikx} dk = -\frac{2\pi i \mathrm{F}(\kappa + i\mu_1)}{f'(\kappa + i\mu_1)} e^{i\kappa x - \mu_1 x} - i \int_0^\infty \frac{\mathrm{F}(-im)}{f(-im)} e^{mx} dm, \quad (7)$$

or, in the limit,

$$\int_0^\infty \frac{\mathrm{F}(k)}{f(k)} e^{ikx} dk = -\frac{2\pi i \mathrm{F}(\kappa)}{f'(\kappa)} e^{i\kappa x}, \quad \cdots \quad (8)$$

when x is considerable. If $\mu_1 > 0$, we have

$$\int_0^\infty \frac{\mathrm{F}(k)}{f(k)} e^{ikx} dk = 0, \quad \cdots \cdots \quad (9)$$

in the same approximate sense.

It is to be remembered, however, that the integrals which we have neglected may be important for small values of x, and may even become infinite for $x = 0$. The infinity may be avoided by the insertion of a factor e^{-zb} in the value of $\mathrm{F}(z)$; this leads to a factor e^{-imb} under the integral sign in the last term of (2), and so secures convergence by fluctuation. This artifice has moreover a physical justification, as enabling us to represent the effect of a force which is diffused about a point, instead of being absolutely concentrated.

The integrals, as thus modified, will still be sufficiently important to be taken into account when x is small. In the application to one-dimensional wave-propagation this is of no great consequence, as the matter only relates to the state of things in the immediate neighbourhood of the source of disturbance. In the problems now to be considered, however, the point requires attention.

2. Proceeding now to our question of wave-propagation in two dimensions, an impulse of the type $\mathrm{J}_0(k\varpi)$, where ϖ denotes distance from a point Q, will give rise to an annular wave-system of the type

$$\zeta = \mathrm{J}_0(k\varpi)\phi(k)e^{i\sigma t} \quad \cdots \cdots \quad (10)$$

about Q as centre. The form of $\phi(k)$, and of σ as a function

of k, will be determined by the nature of the medium. For instance, in the case of water-waves we have

$$\phi(k) = ik/\rho\sigma, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where ρ is the density, whilst

$$\sigma^2 = gk, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

if the depth be great.

It follows from (10) by a theorem of C. Neumann that the effect of a unit impulse concentrated in a point at Q will be
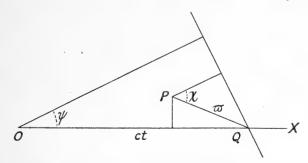
$$\zeta = \frac{1}{2\pi} \int_0^\infty e^{i\sigma t} J_0(k\varpi) \phi(k) k \, dk . \quad . \quad . \quad (13)$$

Since

$$J_0(k\varpi) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{-ik\varpi \cos\chi} d\chi, \quad . \quad . \quad (14)$$

this may be regarded as made up of rectilinear wave-trains whose directions of propagation are distributed uniformly in azimuth about Q.

Suppose now that we have a source of disturbance travelling in the negative direction along the axis of x, with the constant velocity c, and that at the instant under consideration it has reached the origin O. Let Q be its position at any antecedent time t, so that $OQ = ct$. If x, y be the

coordinates of any point P, the distance of P from a rectilinear wave-front through Q will be

$$(ct - x) \cos\psi - y \sin\psi,$$

where ψ denotes the angle which the normal to the wave-front makes with Ox. This expression takes the place of $\varpi \cos\chi$ in (14), and since the integrand is periodic in respect to ψ, with the period 2π, we may replace χ by ψ as independent variable, with the same range of integration.

The effect of an impulse δt delivered at Q is therefore given by

$$\delta\zeta = \frac{\delta t}{4\pi^2}\int_0^\infty\int_{-\pi}^\pi e^{-\mu t+i(\sigma-kc\cos\psi)t+ik(x\cos\psi+y\sin\psi)}\phi(k)k\,dk\,d\psi, \quad (15)$$

the factor $e^{-\mu t}$ being introduced as in the former paper to represent the effect of slight dissipative forces. Integrating from $t=0$ to $t=\infty$, we have

$$\zeta = \frac{1}{4\pi^2}\int_0^\infty\int_{-\pi}^\pi \frac{e^{ik(x\cos\psi+y\sin\psi)}\phi(k)\,k\,dk\,d\psi}{\mu-i(\sigma-kc\cos\psi)}. \quad . \quad (16)$$

3. The approximate integration with respect to k is effected by means of the formulæ of §1. Let κ be a value of k satisfying the equation

$$\sigma = kc\cos\psi, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where ψ must of course lie between $\pm\pi$. That is, $2\pi/\kappa$ is the wave-length corresponding to the wave-velocity $c\cos\psi$. It may of course happen in particular cases that there is no such value of k, or there may be more than one, as in the case of waves in superposed liquids treated in the former paper, or in that of waves under the joint influence of gravity and capillarity. In the latter event each such value will give rise to a separate term in the value of ζ.

Taking for definiteness the case of a single root of (17), the denominator in (16) will vanish, if μ be small, for $k=\kappa+i\mu_1$, approximately, where

$$\mu_1 = \mu/(c\cos\psi-\mathrm{U}), \quad . \quad . \quad . \quad . \quad (18)$$

U being the value which the group-velocity $(d\sigma/dk)$ assumes for $k=\kappa$. Hence, referring to (5) and (9), we have, if $\mathrm{U} < c\cos\psi$,

$$\zeta = \frac{1}{2\pi}\int \frac{e^{i\kappa(x\cos\psi+y\sin\psi)}\kappa\phi(\kappa)d\psi}{c\cos\psi-\mathrm{U}}, \quad . \quad . \quad . \quad (19)$$

where the range of integration is to include only such values of ψ, within the limits $\pm\frac{1}{2}\pi$, as make

$$x\cos\psi+y\sin\psi > 0 \quad . \quad . \quad . \quad . \quad . \quad (20)$$

If, on the other hand, $\mathrm{U} > c\cos\psi$, we have

$$\zeta = \frac{1}{2\pi}\int \frac{e^{i\kappa(x\cos\psi+y\sin\psi)}\kappa\phi(\kappa)d\psi}{\mathrm{U}-c\cos\psi}, \quad . \quad . \quad . \quad (21)$$

the range now including such values as make

$$x\cos\psi+y\sin\psi < 0. \quad . \quad . \quad . \quad . \quad (22)$$

The frictional coefficient has been finally put $=0$, but it may sometimes be necessary to retain it, in order to secure the determinateness of the integrals. This necessity will arise whenever $U - c \cos \psi$ vanishes within the range of ψ, as for instance in the case of water-waves subject to gravity and capillarity combined, if c exceeds the minimum wave-velocity.

It is to be remarked, moreover, that we have so far imagined the disturbing influence to be concentrated at a point, with the result that the integrals with respect to m which we have discarded become in some applications infinite when $x \cos \psi + y \sin \psi = 0$.

This may be remedied by the introduction of a factor e^{-kb} in (13) and subsequent formulæ. The effect of this is that the distribution of the disturbing force is now given by the formula

$$\frac{1}{2\pi} \int_0^\infty J_0(k\varpi) e^{-kb} k \, dk = \frac{b}{2\pi (b^2 + \varpi^2)^{\frac{3}{2}}}, \qquad . \quad (23)\,^*$$

the factors being adjusted to make the integral amount unity. The degree of concentration varies inversely as b.

The modified integrals with respect to m may still be important when $x \cos \psi + y \sin \psi$ is small; but if any prescribed standard of smallness be imposed the range of ψ for which this is satisfied becomes narrower the larger the value of $\sqrt{(x^2 + y^2)}$. It results that the terms in question, after integration with respect to ψ, become negligible at a sufficiently great distance from the origin. It is not easy to do more than indicate in this way the course of the argument in the general case. The particular case of gravity waves will be examined more in detail presently (§7).

4. The definite integrals in (19) and (21) may now be evaluated approximately by Kelvin's method †. If we write, for shortness,

$$\kappa (x \cos \psi + y \sin \psi) = f(\psi), \qquad . \quad . \quad . \quad (24)$$

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* Obtained by differentiating with respect to b the identity

$$\int_0^\infty J_0(k\varpi) e^{-kb} dk = \frac{1}{\sqrt{(b^2 + \varpi^2)}}.$$

† *Proc. Roy. Soc.* vol. xlii. p. 80 (1887); *Math. & Phys. Papers*, vol. iv. p. 303. Reference is however due to Stokes who had briefly indicated the method, as an alternative to one which he actually employed, in a footnote to his paper of 1850 on Airy's integral and other functions. (See his collected "Papers," vol. ii. p. 341.)

and put $\psi = \theta + \omega$, where θ is a root of

$$f'(\theta) = 0, \quad \cdots \quad \cdots \quad (25)$$

we have

$$f(\psi) = f(\theta) + \frac{1}{2}\omega^2 f''(\theta) + \cdots \quad \cdots \quad (26)$$

Owing to the oscillations in sign of the periodic function, the most important part of the integral is that for which the argument is nearly stationary, *i. e.* for which ω is small. The variation of ψ in the remaining factors of the integrand is therefore neglected, and the range of ω may at the same time be extended to $\pm\infty$ without serious error, since only mutually destructive elements are on the whole thus introduced.

Hence in the case of (19) for example we obtain

$$\zeta = \frac{1}{\sqrt{(2\pi)}} \frac{\kappa\phi(\kappa)e^{i\kappa(x\cos\theta + y\sin\theta) \pm \frac{1}{4}i\pi}}{(c\cos\theta - \mathrm{U})\sqrt{|f''(\theta)|}}. \text{ or } 0, \quad . \quad (27)$$

according as $x\cos\theta + y\sin\theta \gtrless 0$. This is in virtue of the formula

$$\int_{-\infty}^{\infty} e^{\pm ia^2\omega^2}d\omega = \frac{1+i}{a}\sqrt{\left(\frac{1}{2}\pi\right)} \quad . \quad . \quad (28)$$

The sign to be prefixed to $\frac{1}{4}i\pi$ in (27) must be that of $f''(\theta)$. The diffusion-factor $e^{-\kappa b}$ may be supposed included, if necessary, in the value of $\phi(\kappa)$.

The locus of points where ζ is in any assigned phase is therefore given by an equation of the type

$$\kappa(x\cos\theta + y\sin\theta) = \text{const.}, \quad . \quad . \quad (29)$$

provided θ be determined as a function of x, y by the relation

$$\frac{d}{d\theta}\kappa(x\cos\theta + y\sin\theta) = 0, \quad . \quad . \quad . \quad (30)$$

κ being known as a function of θ from the fact that $2\pi/\kappa$ is the wave-length corresponding to the wave-velocity $c\cos\theta$.

In other words, the locus in question is the envelope of the straight line

$$x\cos\theta + y\sin\theta = p, \quad . \quad . \quad . \quad . \quad (31)$$

where

$$p = n\lambda, \quad . \quad . \quad . \quad . \quad . \quad (32)$$

λ being the wave-length just defined, and n a numerical coefficient which changes by unity in passing from one curve to the next of the same phase. This is in agreement with the results of the more synthetic investigation [*].

* Lamb, 'Hydrodynamics,' 4th ed., Art. 256.

To calculate $f''(\theta)$ we have

$$\frac{f'(\theta)}{f(\theta)} = \frac{1}{\kappa}\frac{d\kappa}{d\theta} - \frac{x\sin\theta - y\cos\theta}{x\cos\theta + y\sin\theta}, \quad \cdot \quad \cdot \quad \cdot \quad (33)$$

and thence, having regard to (25),

$$\frac{f''(\theta)}{f(\theta)} = -1 - \kappa\frac{d^2}{d\theta^2}\left(\frac{1}{\kappa}\right). \quad \cdot \quad \cdot \quad \cdot \quad (34)$$

We may therefore write in (27)

$$f''(\theta) = -2n\pi\left(1 + \kappa\frac{d^2}{d\theta^2}\kappa^{-1}\right). \quad \cdot \quad \cdot \quad (35)$$

5. As a first application of our results we may take for simplicity an imaginary case, which has, however, already been used for illustrative purposes [*]. A medium is assumed to be such that the group-velocity in it is constant, so that

$$\sigma = \sigma_0 + kU. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (36)$$

Hence

$$\kappa = \frac{\sigma_0}{c\cos\theta - U}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (37)$$

showing that the wave-system is limited by the condition $\cos\theta > U/c$. The equation (32) which determines the configuration of the wave-ridges becomes

$$p = \frac{2\pi n}{\sigma_0}(c\cos\theta - U) \cdot \quad \cdot \quad \cdot \quad \cdot \quad (38)$$

The ridges therefore form a system of circular arcs, of radii $2\pi nU/\sigma_0$, lying to the right of O and convex to it, and touching two straight lines drawn from O at angles $\pm\sin^{-1}(U/c)$ to the axis of x.

6. In the case of a pressure-point moving over the surface of deep water we have, if capillarity be neglected,

$$\kappa = \frac{g}{c^2\cos^2\theta}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (39)$$

The equation of the "isophasal" lines, as they are called by Kelvin, therefore takes the form

$$p = \frac{2n\pi c^2}{g}\cos^2\theta. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (40)$$

[*] Schuster, 'Optics,' 2nd ed. pp. 333-4.

Since the group-velocity is always one-half the wave-velocity, we have

$$U = \frac{1}{2} c \cos \theta, \quad \ldots \ldots \quad (41)$$

so that the formula (27) applies. The proviso

$$x \cos \theta + y \sin \theta > 0$$

shows moreover that the wave-system lies to the right of O, *i. e.* it follows the disturbing agent. The formula (40) leads to the well-known wave-pattern [*] of transverse and diverging waves.

Again, from (35) and (39)

$$f''(\theta) = 2n\pi(1 - 2 \tan^2 \theta). \quad \ldots \quad (42)$$

Taking the value of $\phi(k)$ from (11), it appears that along an isophasal line the elevation due to a travelling pressure of integral amount unity is

$$\zeta = \frac{ig}{\sqrt{n\pi\rho c^4}} \cdot \frac{\sec^4 \theta}{\sqrt{\left|\frac{1}{2} - \tan^2 \theta\right|}} \cdot e^{\left(2n \pm \frac{1}{4}\right)i\pi}, \quad . \quad (43)$$

of which the real part is of course to be retained. The upper sign in the exponential relates to that branch of the curve (40) for which $\tan^2 \theta < \frac{1}{2}$, and the lower to that for which $\tan^2 \theta > \frac{1}{2}$. There is accordingly a difference of phase of a quarter-period between the transverse and diverging waves in the neighbourhood of the cusps. This was first remarked by Kelvin, in 1905 [†]. The law of height which he gave in the paper referred to differs, however, somewhat from (43), owing to the fact that his source of disturbance was constructed by superposition of *lines* or narrow *bands* of pressure distributed uniformly in azimuth about a point. This does not give a strictly localized pressure. Mathematically the effect is equivalent to the omission of the factor k in (13) and subsequent formulæ.

The formula (43) makes ζ infinite for $\tan^2 \theta = \frac{1}{2}$, *i. e.* at the cusps where the two systems of waves coalesce, and again for $\theta = \pm \frac{1}{2}\pi$. The former infinity is a mathematical accident, due to the failure of our approximation through the vanishing of $f''(\theta)$ in (26). The calculation might be

[*] 'Hydrodynamics,' Art. 256. The pattern was first investigated by Kelvin in 1887 ; see his ' Popular Lectures,' vol. iii. p. 482.
[†] Math. and Phys. Papers, vol. iv. p. 412.

amended by continuing the expansion in (26) a step further, and using the formula *

$$\int_{-\infty}^{\infty} e^{ia^3\omega^3}d\omega = \frac{\Pi\left(-\frac{2}{3}\right)}{\sqrt{3}}. \quad . \quad . \quad . \quad (44)$$

The infinity which occurs when $\theta = \pm\frac{1}{2}\pi$ is due to the concentration of the source. If we introduce a diffusion-factor e^{-kb} in our formulæ, as already explained, the second factor in (43) is replaced by

$$\frac{e^{-gb/c^2 \cdot \sec^2\theta}\sec^4\theta}{\sqrt{\left|\frac{1}{2}-\tan^2\theta\right|}}, \quad . \quad . \quad . \quad . \quad (45)$$

which *vanishes* at the places in question.

7. It is possible in a definite problem such as the present to estimate the importance of the terms which were omitted in the integration with respect to k in § 3.

Putting

$$\phi(k) = ike^{-kb}/\rho\sigma, \quad \sigma^2 = gk, \quad . \quad . \quad . \quad (46)$$

in (16), we have to consider the integral

$$\int_0^{i\infty} \frac{e^{izp-zb}z\,dz}{1-g^{-\frac{1}{2}}cz^{\frac{1}{2}}\cos\psi}, \quad . \quad . \quad . \quad (47)$$

taken along the imaginary axis, p being written in place of $x\cos\psi + y\sin\psi$, and μ put $= 0$. This is equivalent to

$$-\int_0^{\infty} \frac{e^{-(p+ib)m}m\,dm}{1-g^{-\frac{1}{2}}c(im)^{\frac{1}{2}}\cos\psi}. \quad . \quad . \quad (48)$$

The important part of this integral is due to comparatively small values of m, so that the second term in the denominator may be omitted. We thus obtain

$$-\frac{1}{(p+ib)^2}, \text{ or } -\frac{1}{(x\cos\psi + y\sin\psi+ib)^2}, \quad . \quad (49)$$

this being, in fact, the first term in the asymptotic expansion of (48) by the usual method. The result has to be integrated with respect to ψ. Since

$$\int_{-\pi}^{\pi}\frac{d\psi}{x\cos\psi + y\sin\psi+ib} = \int_{-\pi}^{\pi}\frac{d\eta}{r\cos\eta+ib} = -\frac{2\pi i}{\sqrt{(r^2+b^2)}}, (50)\dagger$$

* Havelock, Proc. Roy. Soc. A. vol. lxxxi. p. 422 (1908).

† The equality of the second and third members is established by putting $t = \tan\frac{1}{2}\eta$, and integrating over the contour of the upper half of the t-plane, having regard to the singularity at $t = e^{ia}$, where $a = \tan^{-1}(b/r)$.

where $r = \sqrt{(x^2 + y^2)}$, we have, by differentiation with respect to b,

$$\int_{-\pi}^{\pi} \frac{d\psi}{(x \cos \psi + i \sin \psi + ib)^2} = -\frac{2\pi b}{(r^2 + b^2)^{\frac{3}{2}}}. \quad \cdot \quad (51)$$

Inserting the various constant factors that have been omitted, we find that the part of the value of ζ which has been omitted has the value

$$\frac{i}{2\pi g \rho} \frac{b}{(r^2 + b^2)^{\frac{3}{2}}}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (52)$$

This is negligible when the distance r from the origin is large compared with b.

8. When the velocity c of the travelling agent is sufficiently small the influence of capillarity predominates over that of gravity. Taking account of it alone we have

$$\kappa = \frac{\rho c^2}{T} \cos^2 \theta, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (53)$$

where T is the surface-tension. The forms of the isophasal lines are accordingly determined by

$$p = \frac{2n\pi T}{\rho c^2} \sec^2 \theta, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (54)$$

giving a quasi-parabolic shape. Since

$$U = \frac{3}{2} c \cos \theta, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (55)$$

the formula (27) is now to be replaced by that derived from (21) in a similar manner. The approximation makes ζ vanish unless $x \cos \theta + y \sin \theta$ in negative, so that the head ($\theta = 0$) of the wave-system lies to the left of O, *i. e.* it *precedes* the disturbing agent.

Again, by (35) we have, along an isophasal,

$$f''(\theta) = -6n\pi(1 + 2\tan^2 \theta). \quad \cdot \quad \cdot \quad \cdot \quad (56)$$

The final result takes the comparatively simple form

$$\zeta = \frac{1}{\sqrt{n\pi T}} \cdot \frac{1}{\sqrt{(3 + 6\tan^2 \theta)}} \cdot e^{\left(2n + \frac{1}{4}\right)i\pi}. \quad \cdot \quad (57)$$

LXVI. *The Variation of Thermionic Currents with Potentials.* *By* Horace Lester, *Ph.D., Instructor in Physics, Princeton University* *.
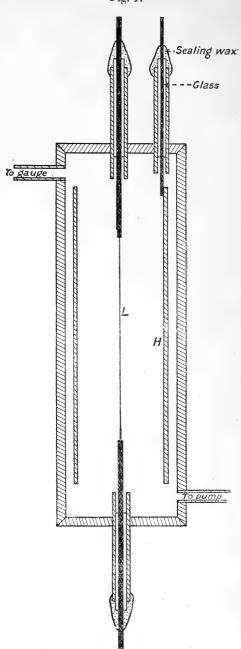
INITIAL thermionic currents from hot surfaces differ from the currents found after steady conditions have been obtained. The peculiarities of these currents have been studied by several investigators. Richardson † found that the positive emission was not permanent, that it did not "saturate" easily, and that the currents increased with the temperature according to an exponential law, at least for a limited range of temperature. He found the carriers to be of atomic magnitude, and considered them to be produced by thermal dissociation of impurities in the hot anode. A further investigation of the initial positive emission has been undertaken more recently by Richardson and Sheard. They were prevented from completing their experiments, but a preliminary account ‡ of the results obtained has been published in a note in the 'Physical Review.' They found that the positive currents decayed with time, the rate of decay depending on the temperature, and that the current-potential relation at constant temperature followed a steep curve up to about 40 volts, at which point a bend occurred towards the potential axis, and beyond which there was a nearly linear increase up to 400 volts. According to Richardson's theory referred to above one would expect saturation to occur at much lower potentials than those mentioned, since the number of negative ions or electrons present is negligible. Saturation for positive currents does not ordinarily occur, although Richardson and Sheard found that with time the slope of the curve above 40 volts decreased ; so that approximate saturation was obtained eventually.

At the suggestion of Professor Richardson, the writer undertook the continuation of this investigation. As a result, the above-mentioned peculiarities of the current-voltage curves for the initial positive emissions have been confirmed, and similar phenomena have been found to occur with the initial negative currents. The further conclusion of Richardson and Sheard that the increase in the current beyond 40 volts is due to secondary ionization caused by the bombardment of a film at the opposite electrode has not been verified. It is possible that such an effect may occur, but it seems clear

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* Communicated by Prof. O. W. Richardson, F.R.S.
† Phil. Mag. July 1903, Sept. 1904.
‡ Phys. Rev. vol. xxxiv. p. 392 (1912).

Fig. 1.
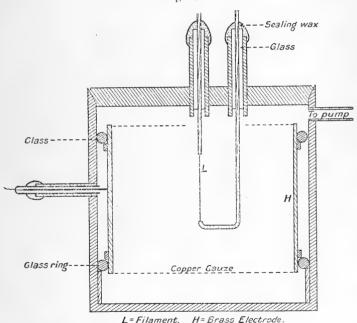
L = Filament.   H = Brass Electrode.

from the experiments that it is not a necessary cause of the increase, and that it cannot have caused any considerable fraction of the increase observed in the present experiments. A number of other points connected with initial thermionic emissions have been examined in the course of the investigation.

The experimental investigation involved observations of thermionic currents in good vacua for various temperatures and potentials, and with various other conditions to be described below. The currents were obtained from platinum wires mounted axially in cylindrical vessels, which contained the receiving electrodes. Figs. 1 and 2 show two types of

Fig. 2.

L = Filament.   H = Brass Electrode.

vessel used. The currents were measured by an electrometer in the ordinary way. For large currents the electrometer was shunted across a resistance, and in some cases a microammeter was used. Generally speaking, the currents were chosen so as to be as large as possible subject to the decay being negligible during the course of the observations. The vacua were produced by a rotary mercury-pump, and were usually about 3×10^{-5} mm. of mercury on the McLeod gauge.

Experimental Results.

In the beginning it was found that lack of saturation characterized both positive and negative currents apparently without distinction. The potential-current curve showed a sharp bend towards the potential axis at about 40 volts. The increase at 400 volts over the value at 40 volts divided by the latter represents fairly the difficulty of attaining saturation. The lack of saturation will be represented by the expression $\frac{\Delta i}{i}$, where i is the current at 40 volts and Δi is the increase in i between 40 and 400 volts.

This extra current may be due to ionization at the surface of the cold electrode, to ionization of a gas or vapour layer near the hot surface, or to phenomena at the surface of the hot electrode. In order to test the first possibility, an apparatus was constructed whereby it was possible to rub the inner surface of the receiving electrode with emery-cloth. Readings could be obtained within 30 seconds after rubbing. This treatment showed no appreciable change in the value of $\frac{\Delta i}{i}$. Another apparatus was designed in which it was possible to heat the cold electrode to approximately 700° C. While the electrode was being heated the platinum wire was cold, and was drawn completely out of the experimental chamber. Repeated heatings, some of several hours' duration, showed no change in the lack of saturation. Another test was carried out as follows :—Experience has shown that after considerable heating the value of $\frac{\Delta i}{i}$ becomes very small, at least in many cases. If $\frac{\Delta i}{i}$ is due to the ionization of the film at the surface of the cold electrode, then the film having been destroyed by one wire, $\frac{\Delta i}{i}$ should be permanently small for a second wire not previously heated. Three or four tests of this sort showed that the value of $\frac{\Delta i}{i}$ for the second wire was independent of the value of $\frac{\Delta i}{i}$ for the first wire. The series of experiments seemed to show conclusively that ionization at the cold electrode of a volatile film could not account for the observed lack of saturation.

To test the second possibility—viz., that lack of saturation was due to ionization in a dense vapour near the hot surface—a wire was mounted in a glass cylinder containing a cylindrical receiving electrode and a quantity of coconut-charcoal in a space below the open end of the cylindrical electrode. Liquid air could be applied to the charcoal and also to a trap in the pump-connexion just outside the glass cylinder. Observations were taken with liquid air off and on the charcoal, off and on the trap, and off and on both together. There was no detectable change in the value of $\frac{\Delta i}{i}$. The pressure on the McLeod gauge was 1×10^{-5} before applying liquid air, and no change occurred upon applying the liquid air. No change in the gauge-reading was expected, however, because the vapour, if it existed, would condense on the colder portions of the tube before it reached the gauge. The result of this experiment indicated that there could be no considerable amount of vapour around the hot surface. The fact that there was no appreciable cooling of the hot wire when liquid air was applied was a further indication that there was very little gas present.

Since the first two hypotheses concerning the location of the phenomena causing lack of saturation were apparently untenable, there remained only the hypothesis that the effect was due to phenomena at the hot surface. To get at the nature of these phenomena, a detailed study of the peculiarities connected with initial emissions was undertaken. In all twenty-three different wires were studied under various conditions of purity, surface-cleanness, pressure, &c. It was known that water vapour actively modifies thermionic currents, so water vapour was in all cases excluded from the apparatus. In parts of the experiments the wires were sprayed with salts, and in some cases they were heavily coated with CaO or BaO.

The results of the series of investigations may be summarized as follows:—In addition to the well-known time decay and variation with potentials, there were two features that characterized all of the emissions studied. The first of these was an initial growth in the value of $\frac{\Delta i}{i}$. This growth was rapid at first, and more gradual later. A stationary value often occurred followed by a period of slow decay. The initial growth was repeated for each succeeding higher temperature. The rate of subsequent decay was more rapid for high than for low temperatures.

The second general effect was a peculiar over-shooting in the current [*]. For a field of 40 volts between the electrodes the currents became steady. Upon changing the potential to 400 volts there was a relatively large current that changed in a few moments to a smaller steady value. The magnitude of the initial current was often 150 per cent. of the steady value. The change occurred mostly in the first 20 seconds, and the total change took about ten minutes in most cases. Upon changing potentials from 400 to 40 volts there was an initially small current that *rose* to a steady value. In this case the greater part of the change occurred in the first five minutes, but the steady value was often not established after two hours.
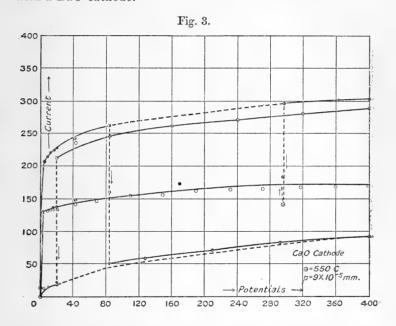
In addition to the above general effects some special investigations established the following facts :—(1) Wires cleaned by boiling for a long time in HNO_3, wires not so treated, and wires purposely contaminated with dust from the floor of the room behaved essentially the same as regards the phenomenon of lack of saturation. Wires known to be very pure in most cases showed currents of smaller magnitude and smaller values of $\frac{\Delta i}{i}$, and smaller over-shooting effects than wires known to be impure. However, there were some exceptions. For instance, the largest value of $\frac{\Delta i}{i}$ obtained was from a very pure wire. Its magnitude was 33 for negative and 27 for positive currents. The value of $\frac{\Delta i}{i}$ ranged from ·1 to 25 for most wires, the most common values being between 10 and 15 for impure wires and between 2 and 7 for pure wires. For impure wires the over-shooting was generally large and the time decay small; for pure wires the over-shooting was generally small and the time decay fairly rapid. Wires sprayed with NaOH and KOH behaved essentially the same as unsprayed wires, except for the magnitude of the currents and the temperatures at which emission became noticeable. A wire coated with $CaCl_2$ showed the remarkable property of perfect saturation when first heated, but after an hour the current had decayed 20 per cent., and there was a value of $\frac{\Delta i}{i}$ of magnitude ·3. $\frac{\Delta i}{i}$ was still growing when observations were discontinued.

* Effects similar to this have been recorded by Richardson, Phil. Trans. A. vol. ccvii. p. 29 (1906).

A wire coated with CaO and tested only for negative emissions showed an instability of currents with applied potentials. There were apparently three possible ranges for the current-potential curves. The current broke suddenly from one range to another. The behaviour may be understood best by reference to fig. 3. These double and triple range phenomena were obtained with two other CaO cathodes and with a BaO cathode.

Fig. 3.

It seems to the writer that the facts established in the above experiments fit very well into already proposed theories, if some further assumptions are made as to conditions at the surface. The lack of saturation, the initial growth, and the over-shooting effects are the most general facts to be adapted.

Richardson's theory of negative thermionic emission regards a discontinuity in the potential energy of an electron at the surface of the metal. Since this theory is well established, the probability of the existence of the discontinuity is great. The discovery and direct measurements of the cooling effect by Wehnelt [*] and by Richardson and Cooke[†], and of the heating

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[*] *Ann. der Physik,* [3] vol. xxviii. p. 537 (1909).
[†] Phil. Mag. April and Sept. 1913.

effect by Richardson and Cooke *, have further established the fact of the potential discontinuity. It is probable that this drop of potential takes place in a film at the surface of the metal which has different properties in case of a new wire as compared with one which has been heated for some time. There is considerable evidence for the existence of surface-films. Langmuir†, for example, showed that films exist, and that it is extremely difficult to get rid of them. I have given evidence in another paper of the existence of ionized films, such that an escaping electron must do work against the field produced by the film ‡. It seems to me that a consideration of the conditions in such a film will give an explanation of the peculiarities of initial thermionic currents.

There is evidence to support the idea that a double layer exists in the film even when the metal is cold and has not been heated §. However, during heating the escape of volatile impurities brings new material to the surface, and this material coming in contact with active gases forms chemical compounds, some of which are solid, and add to an old or actually form a new film.

If a positive potential is applied to the hot metal the more loosely held positive ions escape and form the initial large current which shows small values for $\dfrac{\Delta i}{i}$ and negligible over-shooting. This initial current decays rapidly to a smaller value that may be fairly constant for a long time.

The conditions under which the current shows slow decay may be very complicated. It is probable that an equilibrium condition results between the escaping ions and circumstances tending to prevent their escape. The simplest condition that occurs to me is a state in which the ions have to move through neutral material by thermal energy plus the force of the applied field before they are in a favourable position to evaporate. We should then have equilibrium conditions between the rate of formation of ions, the rate of drift to the film surface, and the rate of escape under the accelerating potential. The rate of formation represents an equilibrium condition between the rate at which dissociation occurs and the rate of removal of the ions. It might be

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* Phil. Mag. July 1910 and April 1911.
† Journ. Am. Chem. Soc. xxxv. p. 105.
‡ Phil. Mag. [6] xxxi. p. 197 (1916).
§ The fact that both the heating effect and the cooling effect are increased when active gases are present indicates that similar films exist at both surfaces.

considered that for a long time the ions are formed as fast
as they are removed. The rate of removal depends on the
rate of drift across the film due to thermal energy and to
the applied field. Since the rate of escape is a function of
the rate of drift to the surface, and since the rate of drift
depends on the applied potentials, the emission clearly depends
on the applied potentials. For potentials high enough for
the drift under the applied field to be relatively more im-
portant than the drift due to the thermal energy there
would be a nearly linear relationship between currents and
potentials. This agrees with observation for potentials above
40 volts. For the current below 40 volts emission is a
function principally of the escape due to thermal energy, and
the current-potential curve is analogous to the unsaturated
portion of an electronic current-potential curve. This, again,
agrees with experiment. The initial condition where ions
escape without having to cross a region of neutral material
should give a small value of $\frac{\Delta i}{i}$. The later stage should give
a large value whose magnitude depends upon the thickness
of the film. Hence the observed initial growth in $\frac{\Delta i}{i}$ is
explicable also. It is known that wires may be "aged out."
That is, after sufficient heating no more positive ionic currents
are obtainable. This decay of the positive current corre-
sponds to the using up of ionizable material. Presumably
the film gradually evaporates. The last traces of film, no
doubt, persist for a long time, but in many cases at least the
film becomes very thin. Now observation showed that in all
cases there was a value of $\frac{\Delta i}{i}$ as long as the currents were
obtainable. In most cases the final value was relatively
small, something of the order ·1. In some cases the value of
$\frac{\Delta i}{i}$ was large even to the end.

The over-shooting is also consistent with the theory of
ionization within the surface-film. The escape of ions at, say,
40 volts is a function of the rate of drift to the surface of the
film. Owing to the small velocity of drift with 40 volts
there is a relatively large number of ions near the surface
of the film. If now the rate of drift is accelerated by
changing the potential to 400 volts, there occurs a relatively
large current during the time in which a new equilibrium ion

density in the film is established consistent with the new velocity. Similarly, upon suddenly decreasing the potential from 400 to 40 volts, there is a decreased current during the time that the film "fills up" to an equilibrium density. The fact that equilibrium was established more quickly at high than at low potentials is consistent with the idea that the speed of the ion in the film depends largely upon the applied potential.

The above discussion has considered only positive currents. However, the same film-conditions would produce similar effects for both the positive and the negative emissions. In the case of the negative currents most of the carriers are electrons, since in only a few cases have negative ionic carriers been detected.

The double-range phenomena observed with CaO and BaO cathodes have been observed by Richardson and Cooke for an osmium cathode and by Langmuir for a tungsten cathode. The instability in current was no doubt caused by an instability in the surface-film. Probably the ionized material in the film becomes unstable, so that chemical combination occurs forming new compounds with characteristic emitting properties. The suddenness of the change from one compound to another was surprising. The large changes in current that occurred illustrate the great importance of surface-films in modifying thermionic emission.

Summary.

It has been shown that there is an initial growth in the value of lack of saturation, and that there is a peculiar over-shooting effect. These facts, together with more generally known behaviour of initial thermionic currents, indicate that the observed peculiarities of initial thermionic emission may be explained as due to the influence of ionized surface-films.

Note.

A peculiar phenomenon was observed with a CaO cathode, that for purposes of better observation was mounted in a glass tube which contained a copper gauze anode. After the wire had been under constant temperature, constant pressure, and zero potential for five or six hours, a set of readings for a current-potential curve was taken. Upon changing the potential to 40 volts a blue glow appeared about the cathode, which was brighter at 400 volts, but which disappeared suddenly without affecting the magnitude of the thermionic current. The potential was switched to zero and then put again at 400. The tube lighted very brilliantly. The wire, which had been at about 900° and uniformly bright, became invisible except for a spot about 2 mm. long near the middle of the wire. This spot was dazzling white, and must have been near 1800° C. The thermionic current was too large for the instrument to record. The anode became heated opposite the glowing spot, and some red sparks passed. The walls of the glass tube glowed with a blue fluorescence except for a pattern corresponding to the shadow of the meshes of the gauze which did not show the fluorescent blue. A lateral tube connecting the experimental chamber with a vertical tube running to the pump happened to be just opposite the bright spot. There was a sharply defined fluorescent spot on the vertical tube opposite the open end of the lateral connexion, though this wall was 3 centimetres behind the gauze anode and 4 centimetres from the hot wire. The glow continued approximately two minutes and stopped abruptly. Subsequent investigation showed the CaO cathode to be covered with finely divided copper or copper oxide. Similar discharges were obtained later, but never a second time from the same spot on the wire. They were increasingly hard to stimulate, and after a time ceased altogether. It was found that a rest-period was necessary to get even a second discharge. Similar discharges occurred in another apparatus (the brass apparatus shown in fig. 2) and also with a BaO cathode.

Palmer Physical Laboratory,
    Princeton.
        July 1915.

LXVII. *Note on the Partial Fraction Problem.*
By I. J. Schwatt [*].

TO separate

$$F(x) = \frac{\sum\limits_{\kappa=0}^{n} m_\kappa x^{n-\kappa}}{(x^2+ax+b)^p},$$

where $2p > n$, and $a^2 - 4b < 0$, into partial fractions, using the division method.

Let $\sum\limits_{\kappa=0}^{n-2} Q_{1\kappa} x^{n-2-\kappa}$ denote the quotient and $A_0 x + B_0$ the remainder (which will, at most, be linear) obtained by dividing $\sum\limits_{\kappa=0}^{n} m_\kappa x^{n-\kappa}$ by $x^2 + ax + b$,

then

$$\frac{\sum\limits_{\kappa=0}^{n} m_\kappa x^{n-\kappa}}{(x^2+ax+b)^p} = \frac{\sum\limits_{\kappa=0}^{n-2} Q_{1\kappa} x^{n-2-\kappa}}{(x^2+ax+b)^{p-1}} + \frac{A_0 x + B_0}{(x^2+ax+b)^p}. \quad (1)$$

Clearing of fractions and equating like powers of x, we have ($Q_{\alpha\beta} = 0$, for negative values of β),

$$\left.\begin{aligned}
Q_{1,\kappa} + a Q_{1,\kappa-1} + b Q_{1,\kappa-2} &= m_\kappa \ (\kappa = 0, 1, 2, \ldots, n-2), \\
A_0 + a Q_{1,n-2} + b Q_{1,n-3} &= m_{n-1}, \\
B_0 + b Q_{1,n-2} &= m_n.
\end{aligned}\right\} \quad (2)$$

We then derive

$Q_{10} = m_0$; $Q_{11} = m_1 - a m_0$; $Q_{12} = m_2 - a m_1 + a^2 m_0 - b m_0$;

$Q_{13} = m_3 - a m_2 + a^2 m_1 - a^3 m_0 - b m_1 + 2 b a m_0$;

$Q_{14} = m_4 - a m_3 + a^2 m_2 - a^3 m_1 + a^4 m_0 - b(m_2 - 2 a m_1 + 3 a^2 m_0) + b^2 m_0$;

$Q_{15} = m_5 - a m_4 + a^2 m_3 - a^3 m_2 + a^4 m_1 - a^5 m_0 - b(m_3 - 2 a m_2 + 3 a^2 m_1 - 4 a^3 m_0) + b^2(m_1 - 3 a m_0)$.

We now assume

$$Q_{1\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} m_{\kappa-2\beta-\alpha}, \quad (3)$$

where $\left[\frac{\kappa}{2}\right]$ is the integral part of $\frac{\kappa}{2}$, and we shall prove that this form holds for $Q_{1\,\kappa+1}$.

From (2)

$$Q_{1\,\kappa+1} = m_{\kappa+1} - aQ_{1\,\kappa} - bQ_{1\,\kappa-1}$$

$$= m_{\kappa+1} - a \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} m_{\kappa-2\beta-\alpha}$$

$$- b \sum_{\beta=0}^{\left[\frac{\kappa-1}{2}\right]} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa-1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} m_{\kappa-1-2\beta-\alpha}. \quad (4)$$

Let κ be even, then

$$Q_{1\,\kappa+1} = m_{\kappa+1} + \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa-2\beta} (-1)^{\alpha+1} a^{\alpha+1} \binom{\alpha+\beta}{\beta} m_{\kappa-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\frac{\kappa}{2}-1} (-1)^{\beta+1} b^{\beta+1} \sum_{\alpha=0}^{\kappa-2\beta-1} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} m_{\kappa-1-2\beta-\alpha}. \quad (5)$$

Designating the first double summation by s_1 and the second by s_2, then

$$s_1 = \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=1}^{\kappa-2\beta+1} (-1)^\alpha a^\alpha \binom{\alpha+\beta-1}{\beta} m_{\kappa+1-2\beta-\alpha}$$

$$= \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta-1}{\beta} m_{\kappa+1-2\beta-\alpha}$$

$$- \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \binom{\beta-1}{\beta} m_{\kappa+1-2\beta},$$

but the last summation is equal to $m_{\kappa+1}$, since if $\beta \neq 0$, $\binom{\beta-1}{\beta} = 0$.

Therefore

$$s_1 = \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta-1}{\beta} m_{\kappa+1-2\beta-\alpha} - m_{\kappa+1} \quad (6)$$

and

$$s_2 = \sum_{\beta=1}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta-1}{\beta-1} m_{\kappa+1-2\beta-\alpha}$$

$$= \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta-1}{\alpha} m_{\kappa+1-2\beta-\alpha}$$

$$- \sum_{\alpha=0}^{\kappa+1} (-1)^\alpha a^\alpha \binom{\alpha-1}{\alpha} m_{\kappa+1-\alpha}.$$

The last summation is equal to $m_{\kappa+1}$, since if $\alpha \neq 0$, $\binom{\alpha-1}{\alpha} = 0$.

Hence

$$s_2 = \sum_{\beta=0}^{\frac{2}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta-1}{\alpha} m_{\kappa+1-2\beta-\alpha} - m_{\kappa+1}. \quad (7)$$

Substituting (6) and (7) in (5) we have

$$Q_{1\,\kappa+1} = \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta-1}{\alpha-1} m_{\kappa+1-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta-1}{\alpha} m_{\kappa+1-2\beta-\alpha} - m_{\kappa+1},$$

$$= \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \left[\binom{\alpha+\beta-1}{\alpha-1} + \binom{\alpha+\beta-1}{\alpha} \right]$$

$$m_{\kappa+1-2\beta-\alpha} - m_{\kappa+1}. \quad \cdot \quad \cdot \quad (8)$$

Now

$$\binom{\alpha+\beta-1}{\alpha-1} + \binom{\alpha+\beta-1}{\alpha} = \binom{\alpha+\beta}{\beta}. \quad \cdot \quad \cdot \quad (9)$$

But if $\alpha = \beta = 0$, (9) is equal to 2. Taking into account $-m_{\kappa+1}$ and remembering that if κ is even $\frac{\kappa}{2} = \left[\frac{\kappa+1}{2} \right]$, (8) becomes

$$Q_{1\,\kappa+1} = \sum_{\beta=0}^{\left[\frac{\kappa+1}{2}\right]} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} m_{\kappa+1-2\beta-\alpha}, \quad (10)$$

which is of the same form as (3).

By a similar method it can be shown that (3) holds also for odd values of κ.

It follows from (2) that A_0 is formed in the same manner as $Q_{1\,n-1}$ (if it existed).

Therefore

$$
\left.
\begin{aligned}
A_0 &= \sum_{\beta=0}^{\left[\frac{n-1}{2}\right]} (-1)^\beta b^\beta \sum_{\alpha=0}^{n-1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} m_{n-2\beta-\alpha-1} \\
\text{and} & \\
B_0 &= m_n - b \sum_{\beta=0}^{\left[\frac{n-2}{2}\right]} (-1)^\beta b^\beta \sum_{\alpha=0}^{n-2-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} m_{n-2\beta-\alpha-2}
\end{aligned}
\right\} . \quad (11)
$$

Again, let $\sum_{\kappa=0}^{n-4} Q_{2\kappa} v^{n-4-\kappa}$ denote the quotient and $A_1 x + B_1$ the remainder (which will, at most, be linear) obtained by dividing $\sum_{\kappa=0}^{n-2} Q_{1\,\kappa} x^{n-2-\kappa}$ by $x^2 + ax + b$, then

$$
\frac{\sum_{\kappa=0}^{n-2} Q_{1\kappa} x^{n-2-\kappa}}{(x^2+ax+b)^{p-1}} = \frac{\sum_{\kappa=0}^{n-4} Q_{2\kappa} x^{n-4-\kappa}}{(x^2+ax+b)^{p-2}} + \frac{A_1 x + B_1}{(x^2+ax+b)^{p-1}}, \quad (12)
$$

where $Q_{2\kappa}$ is the same function of $Q_{1\kappa}$ that $Q_{1\kappa}$ is of m_κ.

Clearing of fractions and equating coefficients of like powers of x, we have

$$
\left.
\begin{aligned}
Q_{2\kappa} &= Q_{1\kappa} - aQ_{2\kappa-1} - bQ_{2\kappa-2} \quad (\kappa=0,\,1,\,2,\,\ldots,\,n-2), \\
A_1 &= Q_{1\,n-3} - aQ_{2\,n-4} - bQ_{2\,n-5}, \\
B_1 &= Q_{1\,n-2} - bQ_{2\,n-4}.
\end{aligned}
\right\} . \quad (13)
$$

We then obtain

$Q_{20} = m_0; \quad Q_{21} = m_1 - 2am_0; \quad Q_{22} = m_2 - 2am_1 + 3a^2m_0 - 2bm_0;$

$Q_{23} = m_3 - 2am_2 + 3a^2m_1 - 4a^3m_0 - 2b(m_1 - 3am_0);$

$Q_{24} = m_4 - 2am_3 + 3a^2m_2 - 4a^3m_1 + 5a^4m_0 - 2b(m_0 - 3am_1 + 4a^2m_0) + 3b^2m_0.$

We now assume

$$
Q_{2\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{5}\right]} (-1)^\beta b^\beta \binom{\beta+1}{1} \sum_{\alpha=0}^{\kappa-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+1}{\beta+1} m_{\kappa-2\beta-\alpha}. \quad (14)
$$

We shall now prove that this form is true for all values of κ.

From (13) follows

$$Q_{2\kappa+1} = Q_{1\kappa+1} - a \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} (-1)^\beta b^\beta \binom{\beta+1}{1} \sum_{\alpha=0}^{\kappa-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+1}{\beta+1} m_{\kappa-2\beta-\alpha}$$

$$- b \sum_{\beta=0}^{\left[\frac{\kappa-1}{1}\right]} (-1)^\beta b^\beta \binom{\beta+1}{1} \sum_{\alpha=0}^{\kappa-1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+1}{\beta+1} m_{\kappa-2\beta-\alpha-1} \quad (15)$$

or

$$Q_{2\kappa+1} = \sum_{\beta=0}^{\left[\frac{\kappa+1}{2}\right]} (-1)^\beta b^\beta \binom{\beta+0}{0} \sum_{\alpha=0}^{\kappa-2\beta+1} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} m_{\kappa-2\beta-\alpha+1}$$

$$+ \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} (-1)^\beta b^\beta \binom{\beta+1}{1} \sum_{\alpha=0}^{\kappa-2\beta} (-1)^{\alpha+1} a^{\alpha+1} \binom{\alpha+\beta+1}{\beta+1} m_{\kappa-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\left[\frac{\kappa-1}{2}\right]} (-1)^{\beta+1} b^{\beta+1} \binom{\beta+1}{1} \sum_{\alpha=0}^{\kappa-1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+1}{\beta+1} m_{\kappa-2\beta-\alpha-1}. \quad (16)$$

Let κ be odd, then

$$Q_{2\kappa+1} = \sum_{\beta=0}^{\frac{\kappa+1}{2}} (-1)^\beta b^\beta \binom{\beta+0}{0} \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} m_{\kappa+1-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\frac{\kappa-1}{2}} (-1)^\beta b^\beta \binom{\beta+1}{1} \sum_{\alpha=0}^{\kappa-2\beta} (-1)^{\alpha+1} a^{\alpha+1} \binom{\alpha+\beta+1}{\beta+1} m_{\kappa-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\frac{\kappa-1}{2}} (-1)^{\beta+1} b^{\beta+1} \binom{\beta+1}{1} \sum_{\alpha=0}^{\kappa-2\beta-1} (-1)^\alpha a^\alpha \binom{\alpha+\beta+1}{\beta+1} m_{\kappa-1-2\beta-\alpha}. \quad (17)$$

Changing in the second double summation α into $\alpha-1$, and β into $\beta-1$ in the third double summation, we have

$$Q_{2\kappa+1} = \sum_{\beta=0}^{\frac{\kappa+1}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} m_{\kappa+1-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\frac{\kappa-1}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta+1} \binom{\beta+1}{1} m_{\kappa+1-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\frac{\kappa+1}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta}{\beta} \beta m_{\kappa+1-2\beta-\alpha} \quad . \quad (18)$$

Adding to the second double summation

$$0 = (-1)^{\frac{\kappa+1}{2}} b^{\frac{\kappa+1}{2}} \sum_{a=0}^{\kappa+1-2\frac{\kappa+1}{2}} (-1)^a a^a \begin{pmatrix} a + \dfrac{\kappa+1}{2} \\ \dfrac{\kappa+1}{2} + 1 \end{pmatrix} \begin{pmatrix} \dfrac{\kappa+1}{2} + 1 \\ 1 \end{pmatrix} m_{\kappa+1-2\frac{\kappa+1}{2}-a}$$

we finally obtain

$$Q_{2\kappa+1} = \sum_{\beta=0}^{\frac{\kappa+1}{2}} (-1)^\beta b^\beta \sum_{a=0}^{\kappa+1-2\beta} (-1)^a a^a m_{\kappa+1-2\beta-a}$$
$$\times \left[\begin{pmatrix} \alpha+\beta \\ \beta \end{pmatrix} + \begin{pmatrix} \alpha+\beta \\ \beta+1 \end{pmatrix} \begin{pmatrix} \beta+1 \\ 1 \end{pmatrix} + \begin{pmatrix} \alpha+\beta \\ \beta \end{pmatrix} \beta \right],$$

or

$$Q_{2\kappa+1} = \sum_{\beta=0}^{\left[\frac{\kappa+1}{2}\right]} (-1)^\beta b^\beta \begin{pmatrix} \beta+1 \\ 1 \end{pmatrix} \sum_{a=0}^{\kappa+1-2\beta} (-1)^a a^a \begin{pmatrix} \alpha+\beta+1 \\ \beta+1 \end{pmatrix} m_{\kappa+1-2\beta-a}, \quad (19)$$

which is of the same form as (14).

In a similar manner it can be shown that (14) holds also for even values of κ.

It follows from (13) that A_1 is formed in the same way as $Q_{1\,n-3}$ (if it existed), therefore

$$A_1 = \sum_{\beta=0}^{\left[\frac{n-3}{2}\right]} (-1)^\beta b^\beta \begin{pmatrix} \beta+1 \\ 1 \end{pmatrix} \sum_{a=0}^{n-3-2\beta} (-1)^a a^a \begin{pmatrix} \alpha+\beta+1 \\ \beta+1 \end{pmatrix} m_{n-3-2\beta-a}$$

and

$$B_1 = \sum_{\beta=0}^{\left[\frac{n-2}{2}\right]} (-1)^\beta b^\beta \begin{pmatrix} \beta+0 \\ 0 \end{pmatrix} \sum_{a=0}^{n-2-2\beta} (-1)^a a^a \begin{pmatrix} \alpha+\beta \\ \beta \end{pmatrix} m_{n-2-2\beta-a}$$

$$- b \sum_{\beta=0}^{\left[\frac{n-4}{2}\right]} (-1)^\beta b^\beta \begin{pmatrix} \beta+1 \\ 1 \end{pmatrix} \sum_{a=0}^{n-4-2\beta} (-1)^a a^a \begin{pmatrix} \alpha+\beta+1 \\ \beta+1 \end{pmatrix} m_{n-4-2\beta-a}.$$

$$\left. \right\} \quad (20)$$

Continuing the process of division we arrive at

$$\left. \begin{aligned} Q_{t\kappa} &= Q_{t-1\,\kappa} - a Q_{t\,\kappa-1} - b Q_{t\,\kappa-2}, \\ A_t &= Q_{t\,n-1-2t} - a Q_{t+1\,n-2-2t} - b Q_{t+1\,n-3-2t}, \\ B_t &= Q_{t-1\,\kappa} - a Q_{t\,\kappa-1} - b Q_{t\,\kappa-2}. \end{aligned} \right\} \quad (21)$$

We now assume

$$Q_{t\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} (-1)^\beta b^\beta \begin{pmatrix} \beta+t-1 \\ t-1 \end{pmatrix} \sum_{a=0}^{\kappa-2\beta} (-1)^a a^a \begin{pmatrix} \alpha+\beta+t-1 \\ \beta+t-1 \end{pmatrix} m_{\kappa-2\beta-a} \quad (22)$$

and show that this form holds for $Q_{t\,\kappa+1}$, $Q_{t+1\,\kappa}$, and $Q_{t+1\,\kappa+1}$.

Substituting $t-1$, $t-2$, $t-3$, ..., 3, 2, 1 for t in

$$Q_{t,\,\kappa+1} = Q_{t-1,\,\kappa+1} - aQ_{t,\,\kappa} - bQ_{t,\,\kappa-1},$$

and adding the resulting equations, we obtain

$$Q_{t,\,\kappa+1} = m_{\kappa+1} - a\sum_{\gamma=1}^{t} Q_{\gamma,\,\kappa} - b\sum_{\gamma=1}^{t} Q_{\gamma,\,\kappa-1}$$

$$= m_{\kappa+1} - a\sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]}\sum_{\alpha=0}^{\kappa-2\beta} (-b)^{\beta}(-a)^{\alpha}m_{\kappa-2\beta-a}\sum_{\gamma=1}^{t}\binom{\beta+\gamma-1}{\beta}\binom{\alpha+\beta+\gamma-1}{\alpha}$$

$$-b\sum_{\beta=0}^{\left[\frac{\kappa-1}{2}\right]}\sum_{\alpha=0}^{\kappa-1-2\beta} (-b)^{\beta}(-a)^{\alpha}m_{\kappa-1-2\beta-a}\sum_{\gamma=1}^{t}\binom{\beta+\gamma-1}{\beta}\binom{\alpha+\beta+\gamma-1}{\alpha}.$$

Now

$$\binom{\beta+\gamma-1}{\beta}\binom{\alpha+\beta+\gamma-1}{\alpha} = \binom{\alpha+\beta}{\beta}\binom{\alpha+\beta+\gamma-1}{\alpha+\beta},$$

therefore

$$\sum_{\gamma=1}^{t}\binom{\beta+\gamma-1}{\beta}\binom{\alpha+\beta+\gamma-1}{\alpha}$$

$$= \binom{\alpha+\beta}{\beta}\sum_{\gamma=1}^{t}\binom{\alpha+\beta+\gamma-1}{\alpha+\beta}$$

$$= \binom{\alpha+\beta}{\beta} \times \text{coefficient of } x^{\alpha+\beta} \text{ in } \sum_{\gamma=1}^{t}(1+x)^{\alpha+\beta+\gamma-1}$$

$$= \binom{\alpha+\beta}{\beta} \times \text{coefficient of } x^{\alpha+\beta+1} \text{ in } \left[(1+x)^{\alpha+\beta+t} - (1+x)^{\alpha+\beta}\right]$$

$$= \binom{\alpha+\beta}{\beta}\binom{\alpha+\beta+t}{t-1}.$$

Hence

$$Q_{t,\,\kappa+1} = m_{\kappa+1} + \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]}\sum_{\alpha=1}^{\kappa+1-2\beta} (-b)^{\beta}(-a)^{\alpha}\binom{\alpha+\beta-1}{\beta}\binom{\alpha+\beta+t-1}{t-1} m_{\kappa+1-2\beta-a}$$

$$+ \sum_{\beta=1}^{\left[\frac{\kappa+1}{2}\right]}\sum_{\alpha=0}^{\kappa+1-2\beta} (-b)^{\beta}(-a)^{\alpha}\binom{\alpha+\beta-1}{\alpha}\binom{\alpha+\beta+t-1}{t-1} m_{\kappa+1-2\beta-a}.$$

If $\alpha=0$ in the first double summation, $\binom{\alpha+\beta-1}{\beta}=0$.
The term corresponding to $\alpha=\beta=0$ is $m_{\kappa+1}$. The upper
limit of β can be written $\left[\frac{\kappa+1}{2}\right]$. If $\beta=0$ is the second
double summation, $\binom{\alpha+\beta-1}{\alpha}=0$.

Therefore

$$Q_{t,\,\kappa+1} = \sum_{\beta=0}^{\left[\frac{\kappa+1}{2}\right]} \sum_{\alpha=0}^{\kappa+1-2\beta} (-b)^\beta (-a)^\alpha \binom{\alpha+\beta+t-1}{t-1} \left\{ \binom{\alpha+\beta-1}{\beta} \right.$$
$$\left. + \binom{\alpha+\beta-1}{\alpha} \right\} m_{\kappa+1-2\beta-\alpha}.$$

Now

$$\binom{\alpha+\beta-1}{\alpha} + \binom{\alpha+\beta-1}{\beta} = \binom{\alpha+\beta}{\beta};$$

and

$$\binom{\alpha+\beta}{\beta} \binom{\alpha+\beta+t-1}{t-1} = \binom{\alpha+\beta+t-1}{\alpha} \binom{\beta+t-1}{\beta}.$$

Hence

$$Q_{t,\,\kappa+1} = \sum_{\beta=0}^{\left[\frac{\kappa+1}{2}\right]} \sum_{a=0}^{\kappa+1-2\beta} (-b)^\beta (-a)^\alpha \binom{\beta+t-1}{\beta} \binom{\alpha+\beta+t-1}{\alpha} m_{\kappa+1-2\ -\alpha}.$$

Therefore, if t is fixed, the assumed form of $Q_{t,\,\kappa}$ is true for all values of κ.

We shall next prove that the assumed form holds also for $Q_{t+1,\,\kappa}$.

We may write

$$Q_{t+1,\,\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} \sum_{a=0}^{\kappa-2\beta} (-b)^\beta (-a)^\alpha \binom{\alpha+\beta}{\beta} Q_{t,\,\kappa-2\beta-\alpha}$$

or

$$Q_{t+1,\,\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} \sum_{a=0}^{\kappa-2\beta} (-b)^\beta (-a)^\alpha \binom{\alpha+\beta}{\beta}$$
$$\times \sum_{\gamma=0}^{\left[\frac{\kappa-2\beta-a}{2}\right]} \sum_{\delta=0}^{\kappa-2\beta-a-2\gamma} (-b)^\gamma (-a)^\delta \binom{\gamma+t-1}{\gamma} \binom{\delta+\gamma+t-1}{\delta}$$
$$\times m_{\kappa-2\beta-a-2\gamma-\delta}.$$

Letting $\alpha = \kappa - 2\beta - \lambda$,

$$Q_{t+1,\,\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} \sum_{\lambda=0}^{\kappa-2\beta} (-b)^\beta (-a)^{\kappa-2\beta-\lambda} \binom{\kappa-\beta-d}{\beta}$$
$$\times \sum_{\gamma=0}^{\left[\frac{\lambda}{2}\right]} \sum_{\delta=0}^{\lambda-2\gamma} (-b)^\gamma (-a)^\delta \binom{\gamma+t-1}{\gamma} \binom{\delta+\gamma+t-1}{\delta} m_{\lambda-2\gamma-\delta},$$

and letting $\delta = \lambda - 2\gamma - \mu$,

$$Q_{t+1,\,\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} \sum_{\lambda=0}^{\kappa-2\beta} (-b)^\beta (-a)^{\kappa-2\beta-\lambda} \binom{\kappa-\beta-\lambda}{\beta}$$

$$\times \sum_{\gamma=0}^{\left[\frac{\lambda}{2}\right]} \sum_{\mu=0}^{\lambda-2\gamma} (-b)^\gamma (-a)^{\lambda-2\gamma-\mu} \binom{\gamma+t-1}{\gamma} \binom{\lambda-\gamma-\mu+t-1}{\gamma+t-1} m_\mu.$$

Since

$$\sum_{\lambda=0}^{\kappa-2\beta} \sum_{\gamma=0}^{\left[\frac{\lambda}{2}\right]} A_{\lambda,\,\gamma} = \sum_{\gamma=0}^{\left[\frac{\kappa}{2}\right]-\beta} \sum_{\lambda=2\gamma}^{\kappa-2\beta} A_{\lambda,\,\gamma},$$

therefore

$$Q_{t+1,\,\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} \sum_{\gamma=0}^{\left[\frac{\kappa}{2}\right]-\beta} (-b)^{\beta+\gamma} (-a)^{\kappa-2\beta-2\gamma}$$

$$\times \sum_{\lambda=2\gamma}^{\kappa-2\beta} \sum_{\mu=0}^{\lambda-2\gamma} (-a)^{-\mu} \binom{\gamma+t-1}{\gamma} \binom{\kappa-\beta-\lambda}{\beta} \binom{\lambda-\gamma-\mu+t-1}{\gamma+t-1} m_\mu.$$

Now

$$\sum_{\lambda=2\gamma}^{\kappa-2\beta} \sum_{\mu=0}^{\lambda-2\gamma} (-a)^{-\mu} \binom{\gamma+t-1}{\gamma} \binom{\kappa-\beta-\lambda}{\beta} \binom{\lambda-\gamma-\mu+t-1}{\gamma+t-1} m_\mu$$

$$= \sum_{\mu=0}^{\kappa-2\beta-2\gamma} (-a)^{-\mu} m_\mu \binom{\gamma+t-1}{\gamma} \sum_{\lambda=\mu}^{\kappa-2\beta-2\gamma} \binom{\kappa-\beta-\lambda}{\kappa-2\beta-\lambda} \binom{\lambda-\gamma-\mu+t-1}{\lambda-2\gamma-\mu},$$

and since

$$\binom{p}{q} = (-1)^q \binom{q-p-1}{q},$$

$$\sum_{\lambda=\mu}^{\kappa-2\beta-2\gamma} \binom{\kappa-\beta-\lambda}{\beta} \binom{\lambda-\gamma-\mu+t-1}{\gamma+t-1} = (-1)^{\kappa-\mu} \sum_{\lambda=\mu}^{\kappa-2\beta-2\gamma} \binom{-\beta-1}{\kappa-2\beta-\lambda} \binom{-\gamma-t}{\lambda-2\gamma-\mu}$$

$$= (-1)^{\kappa-\mu} \times \text{coefficient of } x^{\kappa-2\beta-2\gamma-\mu} \text{ in } (1+x)^{-\gamma-t-\beta-1}$$

$$= (-1)^{\kappa-\mu} \binom{-\gamma-t-\beta-1}{\kappa-2\beta-2\gamma-\mu} = \binom{\kappa-\beta-\gamma+t-\mu}{\kappa-2\beta-2\gamma-\mu}.$$

Therefore

$$Q_{t+1,\,\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} \sum_{\gamma=0}^{\left[\frac{\kappa}{2}\right]-\beta} (-b)^{\beta+\gamma} \sum_{\mu=0}^{\kappa-2\beta-2\gamma} (-a)^{-\mu+\kappa-2\beta-2\gamma}$$

$$\times \binom{\gamma+t-1}{\gamma} \binom{\kappa-\beta-\gamma+t-\mu}{\beta+\gamma+t} m_\mu.$$

Next let $\beta + \gamma = \alpha'$, then

$$Q_{t+1,\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} \sum_{\alpha'=\beta}^{\left[\frac{\kappa}{2}\right]} (-b)^{\alpha'} \sum_{\mu=0}^{\kappa-2\alpha'} (-a)^{\kappa-2\alpha'-\mu} m_\mu \binom{\alpha'-\beta+t-1}{t-1} \binom{\kappa-\alpha'+t-\mu}{\alpha'+t}$$

$$= \sum_{\alpha'=0}^{\left[\frac{\kappa}{2}\right]} (-b)^{\alpha'} \sum_{\mu=0}^{\kappa-2\alpha'} (-a)^{\kappa-2\alpha'-\mu} m_\mu \sum_{\beta=0}^{\alpha'} \binom{\alpha'-\beta+t-1}{t-1} \binom{\kappa-\alpha'+t-\mu}{\alpha'+t}.$$

But

$$\sum_{\beta=0}^{\alpha'} \binom{\alpha'-\beta+t-1}{t-1} = \text{coefficient of } x^{t-1} \text{ in } \sum_{\beta=0}^{\alpha'} (1+x)^{\alpha'-\beta+t-1}$$

$$= \binom{\alpha'+t}{t},$$

therefore

$$Q_{t+1,\kappa} = \sum_{\alpha'=0}^{\left[\frac{\kappa}{2}\right]} (-b)^{\alpha'} \sum_{\mu=0}^{\kappa-2\alpha'} (-a)^{\kappa-2\alpha-\mu} \binom{\alpha'+t}{\alpha'} \binom{\kappa-\alpha'+t-\mu}{\alpha'+t} m_\mu.$$

Letting $\mu = \kappa - 2\alpha' - \beta'$, then

$$Q_{t+1,\kappa} = \sum_{\alpha'=0}^{\left[\frac{\kappa}{2}\right]} (-b)^{\alpha'} \sum_{\beta'=0}^{-2\alpha'} (-a)^{\beta'} \binom{\alpha'+t}{\alpha'} \binom{\alpha'+\beta'+t}{\beta'} m_{\kappa-2\alpha'-\beta'}.$$

Interchanging α' and β' and dropping the prime signs, we have

$$Q_{t+1,\kappa} = \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} \sum_{\alpha=0}^{\kappa-2\beta} (-b)^\beta (-a)^\alpha \binom{\beta+t+1-1}{\beta} \binom{\alpha+\beta+t+1-1}{\alpha} m_{\kappa-2\beta-\alpha}.$$

which is of the same form as the expression for $Q_{t,\kappa}$.

We finally show that (22) holds for $Q_{t+1\,\kappa+1}$.

Now

$$Q_{t+1\,\kappa+1} = Q_{t\kappa+1} - aQ_{t+1\,\kappa} - bQ_{t+1\,\kappa-1}$$

$$= \sum_{\beta=0}^{\left[\frac{\kappa+1}{2}\right]} (-1)^\beta b^\beta \binom{\beta+t-1}{t-1} \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+t-1}{\beta+t-1} m_{\kappa+1-2\beta-\alpha}$$

$$- a \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} (-1)^\beta b^\beta \binom{\beta+t}{t} \sum_{\alpha=0}^{\kappa-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+t}{\beta+t} m_{\kappa-2\beta-\alpha}$$

$$- b \sum_{\beta=0}^{\left[\frac{\kappa-1}{2}\right]} (-1)^\beta b^\beta \binom{\beta+t}{t} \sum_{\alpha=0}^{\kappa-1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+t}{\beta+t} m_{\kappa-1-2\beta-\alpha} \quad (23)$$

$$= \sum_{\beta=0}^{\left[\frac{\kappa+1}{2}\right]} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+t-1}{\beta+t-1} \binom{\beta+t-1}{t-1} m_{\kappa+1-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\left[\frac{\kappa}{2}\right]} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa-2\beta} (-1)^{\alpha+1} a^{\alpha+1} \binom{\alpha+\beta+t}{\beta+t} \binom{\beta+t}{t} m_{\kappa-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\left[\frac{\kappa-1}{2}\right]} (-1)^{\beta+1} b^{\beta+1} \sum_{\alpha=0}^{\kappa-1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+t}{\beta+t} \binom{\beta+t}{t} m_{\kappa-1-2\beta-\alpha}. \quad (24)$$

Let κ be even, then

$$Q_{t+1\,\kappa+1} = \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+t-1}{\beta+t-1} \binom{\beta+t-1}{t-1} m_{\kappa+1-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+t-1}{\beta+t} \binom{\beta+t}{t} m_{\kappa+1-2\beta-\alpha}$$

$$+ \sum_{\beta=0}^{\frac{\kappa}{2}} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+t-1}{\beta+t-1} \binom{\beta+t-1}{t} m_{\kappa+1-2\beta-\alpha}, \quad (25)$$

since the second double summation gives zero terms when $\alpha=0$, and the third double summation gives zero terms when $\beta=0$.

Adding the three double summations in (25) we have

$$Q_{t+1\,\kappa+1} = \sum_{\beta=0}^{\left[\frac{\kappa+1}{2}\right]} (-1)^\beta b^\beta \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha m_{\kappa+1-2\beta-\alpha} \left[\binom{\alpha+\beta+t-1}{\beta+t-1} \binom{\beta+t-1}{t-1} \right.$$

$$\left. + \binom{\alpha+\beta+t-1}{\beta+t} \binom{\beta+t}{t} + \binom{\alpha+\beta+t-1}{\beta+t-1} \binom{\beta+t-1}{t} \right]. \quad (26)$$

But the sum within the brackets equals

$$\frac{(\alpha+\beta+t)\,!}{\alpha!\;\beta!\;t!} = \frac{(\alpha+\beta+t)\,!}{\alpha!\;(\beta+t)!} \frac{(\beta+t)\,!}{\beta!\;t!} = \binom{\alpha+\beta+t}{\beta+t} \binom{\beta+t}{t}. \quad . \quad . \quad . \quad (27)$$

Therefore

$$Q_{t+1\,\kappa+1} = \sum_{\beta=0}^{\left[\frac{\kappa+1}{2}\right]} (-1)^\beta b^\beta \binom{\beta+t}{t} \sum_{\alpha=0}^{\kappa+1-2\beta} (-1)^\alpha a^\alpha \binom{\alpha+\beta+t}{\beta+t} m_{\kappa+1-2\beta-\alpha}. \quad . \quad (28)$$

In a similar manner can be shown that (22) holds for odd values of κ.

It follows from (21) that A_t is formed in the same way as $Q_{t+1\,n-1-2t}$ (if it existed).

Hence

$$
\left.\begin{aligned}
A_t &= \sum_{\beta=0}^{\left[\frac{n-1-2t}{2}\right]} (-1)^\beta b^\beta \binom{\beta+t-1}{t-1} \sum_{\alpha=0}^{n-1-2t-2\beta} (-1)^\alpha a^\alpha \\
&\qquad\qquad\times \binom{\alpha+\beta+t-1}{\beta+t-1} m_{n-2t-2\beta-\alpha-1}, \\[2ex]
\text{and} \\[1ex]
B_t &= \sum_{\beta=0}^{\left[\frac{n-2t}{2}\right]} (-1)^\beta b^\beta \binom{\beta+t-1}{t-1} \sum_{\alpha=0}^{n-2t-2\beta} (-1)^\alpha a^\alpha \\
&\qquad\qquad\times \binom{\alpha+\beta+t-1}{\beta+t-1} m_{n-2t-2\beta-\alpha} \\[1ex]
&-b \sum_{\beta=0}^{\left[\frac{n-2-2t}{2}\right]} (-1)^\beta b^\beta \binom{\beta+t}{t} \sum_{\alpha=0}^{n-2-2t-2\beta} (-1)^\alpha a^\alpha \\
&\qquad\qquad\times \binom{\alpha+\beta+t}{\beta+t} m_{n-2-2t-2\beta-\alpha},
\end{aligned}\right\} \quad . \quad (29)
$$

$A_t x + B_t$ being the numerator of the fraction whose denominator is $(x^2 + ax + b)^{p-t}$.

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GEOLOGICAL SOCIETY.

[Continued from p. 496.]

February 23rd, 1916.—Dr. Alfred Harker, F.R.S., President, in the Chair.

THE following communication was read :—

'On the Origin of some River-Gorges in Cornwall and Devon.' By Henry Dewey, F.G.S.

In North Cornwall, near Tintagel, there is an area of peculiar topography characterized by the presence of an upland plain or

plateau. This plateau is dissected by deep gorges, with their walls scarred by potholes through which the rivers flow in a series of waterfalls, cascades, and rapids.

This plateau is terminated inland by degraded cliffs rising abruptly from 400 feet above sea-level, while the plain slopes gently to the recent sea-cliffs, mostly over 300 feet high. The plateau has been cut across rocks of different degrees of hardness, and is overlain by deposits of detritus and peat. Wherever the plain occurs, the scenery is featureless, and the land boggy and waterlogged.

The widespread occurrence of this plain over Cornwall and Devon at a uniform height suggests that in its final stages it was a plain of marine erosion. The author accepts Mr. Clement Reid's conclusion that its date is not later than Pliocene. Its uplift in post-Pliocene times led to rejuvenescence of the rivers, initiation of coastal cascades, and the production of gorges aided by the formation of potholes.

At Lydford, on the western flank of Dartmoor, the uplift led to the diversion of the Lyd by a stream that breached the valley-side and tapped the head-waters of the river.

A small stream, the Burn, now flows past Was Tor and Brentor, through the valley formerly occupied by the Lyd. The shortened journey to the lowlands bestowed such enhanced cutting-power upon the river that it quickly incised a chasm through which it now flows more than 200 feet below the base of its former valley; while a tributary enters as a waterfall from a hanging valley near Lydford Junction.

The elevation of the land also led to formation of gorges of similar character in other upland plateaux. These plateaux have been described by Mr. Barrow in the Quarterly Journal of the Geological Society, and reference is made to them by the author in connexion with the effects upon them of the uplift.

There are thus in Cornwall and Devon two characteristic types of scenery, to which in great part these counties owe their charm. Wide featureless plains covered with heath and marshland and dominated by tors and crags, on which the drainage is sluggish and vague, alternate with deeply-incised rocky ravines where rivers flow as rapids and cascades. These two types mark successive periods of erosion. Post-Pliocene uplift gave such increased cutting-power to the rivers that they quickly incised chasms in their former valleys, employing while so doing the activity of waterfalls and rapids.

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END OF THE THIRTY-FIRST VOLUME.